THE DESIGN AND SYNTHESIS OF ELECTRONIC MATERIALS BASED ON ARYLAMINES

A Thesis Presented

By

JASON E. FIELD

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Organic Chemistry

May 2003

THE DESIGN AND SYNTHESIS OF ELECTRONIC MATERIALS BASED ON ARYLAMINES

A Thesis Presented

by

JASON E. FIELD

Approved as to style and content by:

Prof. D. Venkataraman, Chair

Prof. P. Lahti, Member

Prof. C. P. Lillya, Member

Prof. P. Bianconi, Member

Prof. M. Tuominen, Member

Prof. B. Jackson, Department Head
Chemistry

DEDICATION

For my wife, Lora.

ACKNOWLEDGEMENTS

I would like to thank my advisor D. Venkataraman (DV), for his guidance, insight, and for sharing his encyclopedic knowledge of chemistry. I thank the entire DV group for their friendship and support.

I would also like to thank the many people who contributed their time, equipment, and advice to this project: my undergraduate students (affectionately known as the “helper monkeys”) Kate Huber, Noah Tremblay, and especially Tom Hill, whose skills as an organic chemist greatly contributed to this research; Catherine Goodman and Hiroshi Nakade for CD data collection; Prof. Vince Rotello for use of his UV spectrometer and fluorimeter; Paul Carrington and Prof. Michael Maroney for assistance with cyclic voltammetry; Lora Field and Prof. Paul Lahti for assistance with ESR; Marianny Combariza and Prof. Richard Vachet for assistance with ESI-MS; and our collaborators Dr. Gilles Muller and Prof. James Riehl at the University of Minnesota Duluth, for sharing their expertise in the field of CPL measurement.

Funding for this project was provided by the University of Massachusetts Amherst start-up funds, NSF CAREER Grant CHE-0134287, and Bristol-Myers Squibb.

I would like to thank all my friends and family that have supported me over my many years as a student. To my parents Richard and Peggy-Ann, thank you for always being there to support me financially, emotionally, and spiritually. To my sisters Rachelle and Nichola, thanks for your constant encouragement. I thank my father- and mother-in-law Marian and Bonnie for their support. I also thank best friends Kevin (a.k.a. Dadoo), Keenan, and Tom for your loyalty and friendship.

And finally, I want to thank my wife Lora, for supporting me in everyway possible. Thank you.

ABSTRACT

THE DESIGN AND SYNTHESIS OF ELECTRONIC MATERIALS BASED ON ARYLAMINES

MARCH 2003

JASON E. FIELD, B. Sc., UNIVERSITY OF WATERLOO

Ph. D., UNIVERSITY OF MASSACHUSETTES, AMHERST

Directed by: Professor D. Venkataraman

Combining the tools of traditional organic synthesis with those of the emerging field of supramolecular chemistry, we have designed several interesting systems based on triarylamines. This moiety has been well established as versatile electroactive group for use in electronic and electro-optic materials. Herein, we report the development of a D_3h triketone building block for potential use in the assembly of higher dimensional electronic solids. We have also developed a series of bridged triarylamines that constitute a new class of electroactive heterohelicenes. Furthermore, we have show that these systems form stable radical cations and have the ability to emit circularly polarized light. Finally, we have demonstrated the ability to direct the solid state structures of arylamines to form zigzag, helical, tetrahedral, and porous architectures.

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (Con't)

Page

APPENDICES

LIST OF FIGURES

LIST OF ABBREVIATIONS

bcc	- body centered cubic
BTMABr$_3$	- benzyltrimethylammonium tribromide
CD	- circular dichroism
CPL	- circularly polarized luminescence
dba	- dibenzylideneacetone
DCC	- N,N’-dicyclohexylcarbodiimide
DHU	- dicyclohexylurea
DMAP	- N,N-dimethylaminopyridine
DPPB	- 1,4-bis(diphenylphosphino)butane
DPPF	- 1,1’-bis(diphenylphosphino)ferrocene
ESI-MS	- electrospray ionization mass spectrometry
ESR	- electron spin resonance
LC	- liquid crystal
LCD	- liquid crystal diode
NMR	- nuclear magnetic resonance
OLED	- organic light emitting diode
PHA	- phenylacridone
R_f	- retention factor
SCE	- standard calomel electrode
TDATA	- 4,4’,4’’-tris(diphenylamino)triphenylamine
TFA	- trifluoroacetic acid
TLC	- thin layer chromatography
TPD	- N,N’-diphenyl-N,N’-bis-*m*-tolylbenzidine
α-NPD	- N,N’-diphenyl-N,N’-bis-α-napthylbenzidine

CHAPTER 1

PROLOGUE

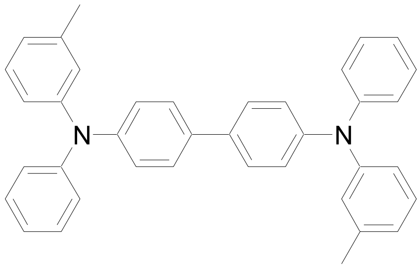
1.1 Introduction:

The development of organic materials for electronic applications has drawn much attention over the last two decades. During this time, there have been significant advances made in this field, leading to the use of organic materials in many present day applications such as xerographic and display technologies.[1] Electronic organic materials have even inspired the development of devices with potential applications such as Field-effect transistors[2] and solar cells.[3] Another area that has revolutionized contemporary science is the growing field of supramolecular chemistry.[4,5] The mission for all supramolecular chemists is to direct the solid state assembly of molecules into desired architectures. Our research interests reside at the interface of these two areas of materials science. Our goal is to use the power of organic synthesis to construct novel electroactive molecules at the molecular level and to direct the assembly of these molecules using intermolecular interactions to create novel electroactive materials at the supramolecular level. By doing so, we hope to gain better control of the macroscopic properties of these materials and thus be able to tune them in a rational manner for a desired application.[6]

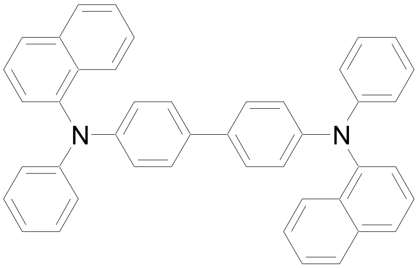
Materials based on arylamines have been extensively studied due to their interesting physical, photochemical, and electrochemical properties.[1,7] These materials tend to form uniform amorphous layers, are highly luminescent chromophores, and can form stable radical cations without undergoing subsequent chemical transformations. Consequently, this class of materials has been widely exploited as hole-transport layers in organic light emitting diodes (OLEDs). In fact, the most commonly used hole-transporting materials for OLED applications are arylamine-based, including N,N'-

diphenyl-N,N'-bis-*m*-tolylbenzidine (TPD), 4,4',4''-tris(diphenylamino)triphenylamine (TDATA), and N,N'-diphenyl-N,N'-bis-α-napthylbenzidine (α-NPD).

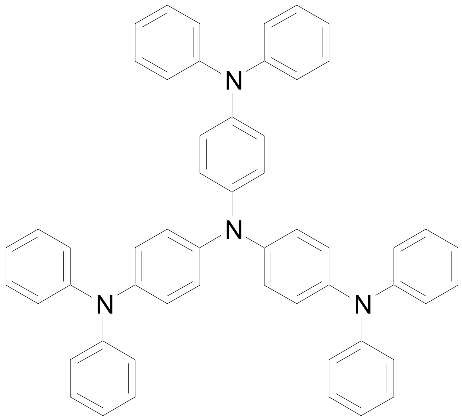
Another advantage to arylamine-based materials is the recent advances in their synthesis. Over the last ten years, Hartwig[8,9] and Buchwald[10,11] have independently developed highly active palladium catalysts for the coupling of arylamines to arylhalides. With high yields, mild conditions, and a tolerance for a wide range of functional groups, this chemistry has made the synthesis of most arylamine-based materials relatively simple. Even more recently, our group and others have reported the ability to do similar coupling reactions using copper catalysts, making these reactions affordable as well as efficient.[12]



TPD



α-NPD



TDATA

With all of the associated advantages of arylamines, we set out to develop new electronic materials based on these systems. This thesis will describe the synthesis of a planar D_{3h} triketone as a building block for a higher dimensional electronic network, the development of a series of bridged triarylamines that constitute a new class of electroactive heterohelicenes, and strategies for the assembly of arylamines in the solid state to form predictable architectures.

1.2 References:

(1) Shirota, Y. "Organic materials for electronic and optoelectronic devices" *J. Mater. Chem.* **2000**, *10*, 1-25.

(2) Schmidt-Mende, L.; Fechtenkotter, A.; Mullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. "Self-organized discotic liquid crystals for high-efficiency organic photovoltaics" *Science* **2001**, *293*, 1119-1122.

(3) Nelson, J. "Solar energy - Solar cells by self-assembly?" *Science* **2001**, *293*, 1059-1060.

(4) Desiraju, G. R. "Supramolecular Synthons in Crystal Engineering - a New Organic- Synthesis" *Angew. Chem. Int. Ed.* **1995**, *34*, 2311-2327.

(5) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. "Molecular Self-Assembly and Nanochemistry - a Chemical Strategy for the Synthesis of Nanostructures" *Science* **1991**, *254*, 1312-1319.

(6) Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. "From molecules to materials: Current trends and future directions" *Adv. Mater.* **1998**, *10*, 1297-1336.

(7) Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. "New triarylamine-containing polymers as hole transport materials in organic light-emitting diodes: Effect of polymer structure and cross-linking on device characteristics" *Chem. Mater.* **1998**, *10*, 1668-1676.

(8) Hartwig, J. F. "Carbon-heteroatom bond-forming reductive eliminations of amines, ethers, and sulfides" *Acc. Chem. Res.* **1998**, *31*, 852-860.

(9) Hartwig, J. F. "Transition metal catalyzed synthesis of arylamines and aryl ethers from aryl halides and triflates: Scope and mechanism" *Angew. Chem. Int. Ed.* **1998**, *37*, 2047-2067.

(10) Muci, A. R.; Buchwald, S. L. "Practical palladium catalysts for C-N and C-O bond formation", *Vol. 219*, **2002**; pp 131-209.

(11) Yang, B. H.; Buchwald, S. L. "Palladium-catalyzed amination of aryl halides and sulfonates" *J. Organomet. Chem.* **1999**, *576*, 125-146.

(12) Gujadhur, R.; Venkataraman, D.; Kintigh, J. T. "Formation of aryl-nitrogen bonds using a soluble copper(I) catalyst" *Tetrahedron Lett.* **2001**, *42*, 4791-4793.

CHAPTER 2

CONSTRUCTION OF HIGHER DIMENSIONAL SOLIDS

2.1 Introduction:

With the ever increasing emphasis for organic-based materials to be used in electronic devices, it is important that scientists address the inherent shortcomings of these systems. One such problem that plagues organic conducting materials is a phenomenon known as Peierls distortion.[1, 2] Peierls distortion can be best described as the solid-state analog of the Jahn-Teller distortion. For example, molecules that have two π-electrons in degenerate molecular orbitals, such as 1,3-cyclobutadiene (Figure 1), have the tendency to distort so as to pair the electrons in a bonding orbital, thus removing the degeneracy and lowering the overall energy of the system. This is an example of a second order Jahn-Teller distortion.

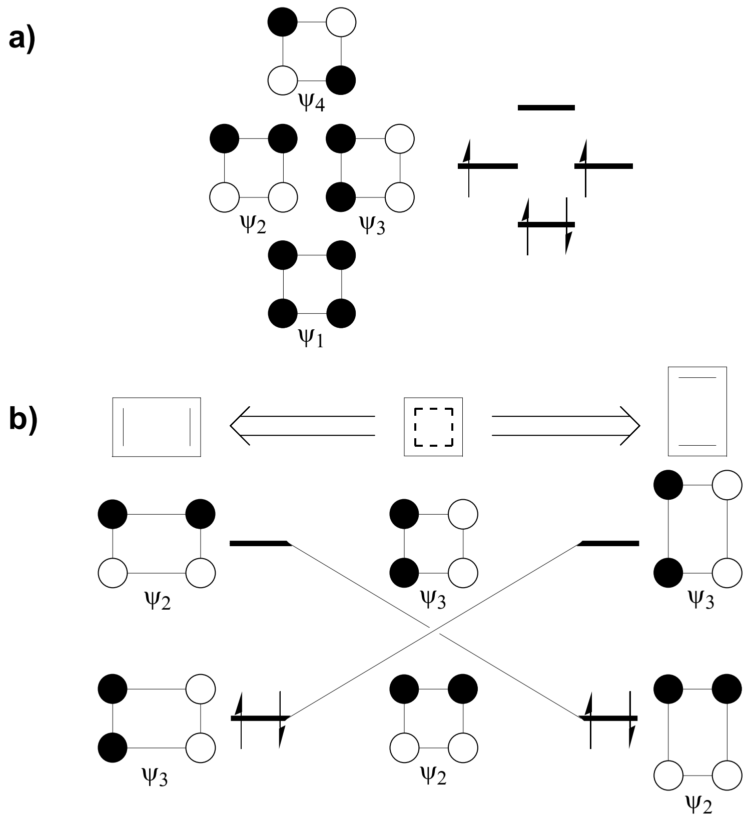


Figure 1. The second-order Jahn-Teller distortion of 1,3-cylcobutadiene. (a) the molecular orbitals of the undistorted molecule and (b) the subsequent distortion by the pairing of the electrons.

The analogous distortion in the solid-state is called Peierls distortion and is best illustrated in polyacetylene (Figure 2). This conjugated polymer is calculated to have metal-like conductivity at very high temperatures. However, at practical temperatures the π-electrons pair, causing a localization of the double bonds.[3] This distortion is characterized by a widening of the band gap of the polymer at the Fermi level, thus making the polymer an insulator.

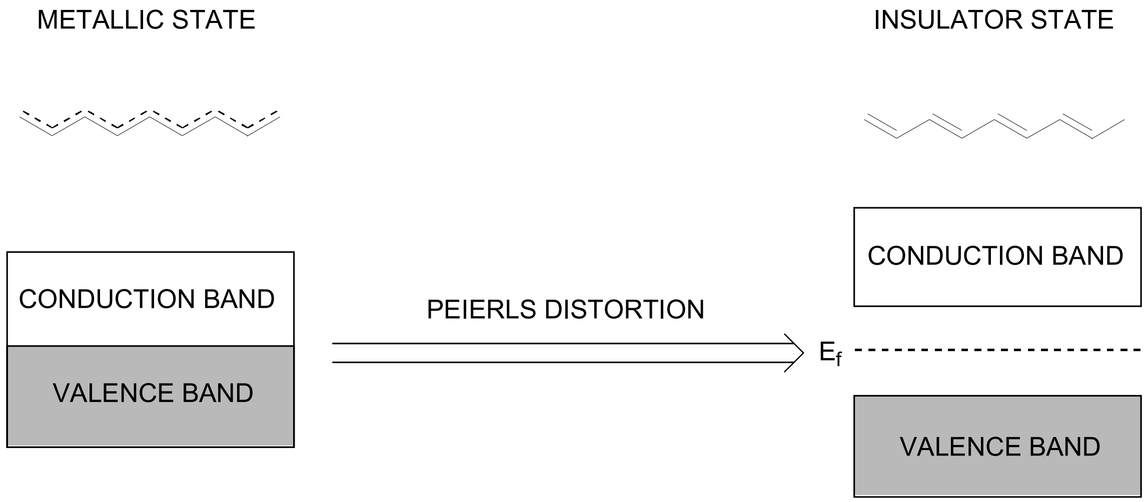


Figure 2. The Peierls distortion as observed in polyacetylene.

The Peierls distortion is most prominent in one-dimensional conductors. It has also been observed that higher-dimensional systems, like graphite (the two-dimensional analog of polyacetylene), tend to suppress this phenomenon.[2] It is this observation that inspired us to pursue the development of a higher-dimensional electronic network. Our approach is to use an electroactive building block of appropriate symmetry and functionality, so that it can assemble in the solid state in a predictable, higher dimensional motif. In essence, we wish to use the tools of supramolecular chemistry to control the solid state arrangement of electroactive molecules.

One of the most well-documented topologies in supramolecular chemistry is that of the hexagonal network. Such a network is readily assembled from building blocks that have supramolecular synthons along a three-fold symmetry axis (Figure 3a). Since our goal is the construction of an electronic solid, the use of an electroactive C_3-symmetric core and charge-transfer interactions are desired. For the core structure, we choose the D_{3h} triketone (Figure 3b), which is based on triarylamine, a moiety that has well documented electronic properties.[4,5] For the charge-transfer interaction, we chose one of the most prominent interactions observed in supramolecular chemistry, the perfluorobenzene and benzene π-stacking interaction.[6]

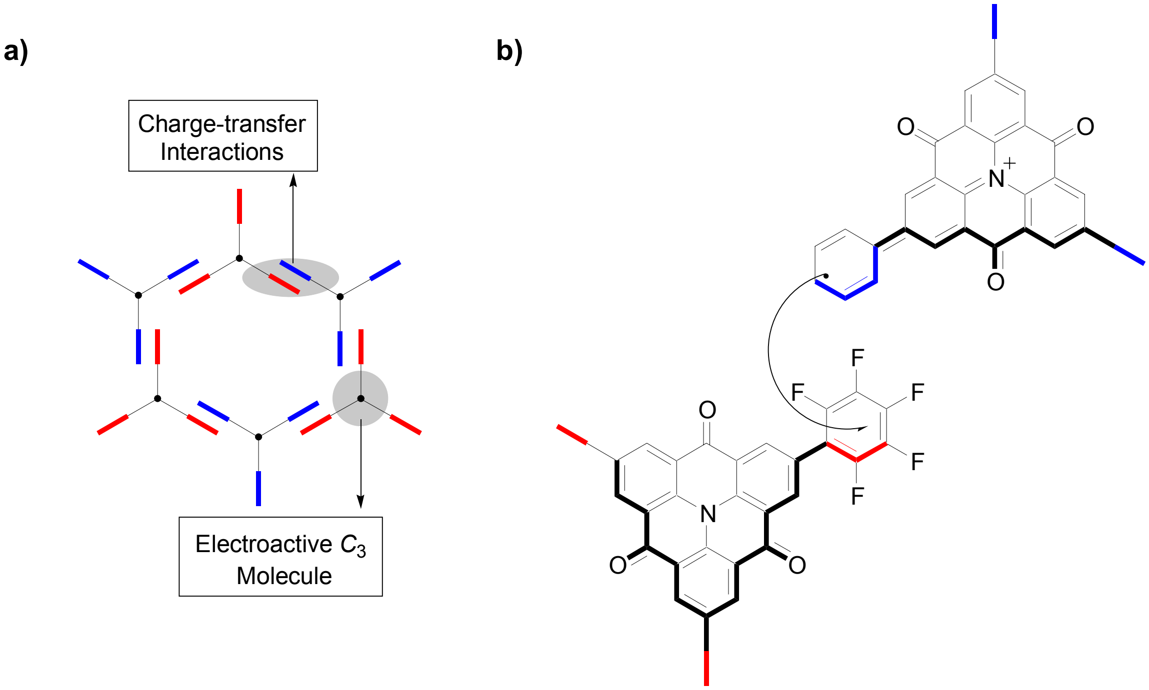


Figure 3. (a) The construction of a two-dimensional hexagonal network and (b) the target D_{3h} triketone building blocks.

2.2 Synthesis:

The only reported synthesis of **3** was by Hellwinkel and Melan in 1971 (Figure 4).[7] In this synthesis, they employed a copper-catalyzed Ullmann-type coupling of methyl anthranilate and methyl 2-iodobenzoate to obtain **1** in a 70% yield. A subsequent Ullmann coupling reaction gave the desired triarylamine **2** in 26% yield. This triarylamine was then cyclized in boiling sulfuric acid to give the final D_{3h} triketone **3** in 37% yield and an overall yield of 6.6% over three steps. Attempts to carry-out the cyclization in polyphosphoric acid resulted in the formation of the decarboxylated product **4** in 44% yield.

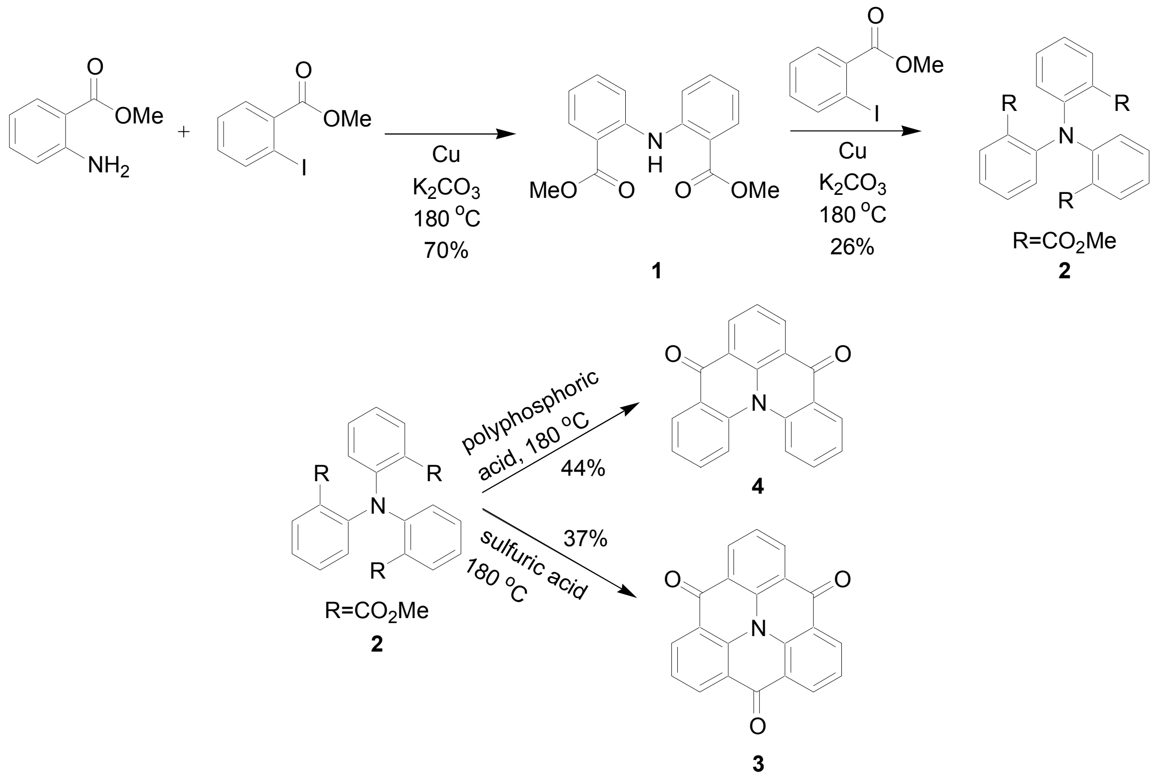


Figure 4. Synthetic procedures reported by Hellwinkel and Melan.

The methodology reported by Hellwinkel and Melan is harsh and low yielding. We believed that it would be possible to improve upon this basic approach by utilizing modern synthetic reactions which were unavailable at the time this procedure was reported. Over the past decade, Hartwig[8,9] and Buchwald[10,11] have independently developed palladium(0) catalysts for the coupling of aryl amines and aryl halides. This methodology provides a vast improvement over the Ullmann-type coupling since these reactions are carried out at much lower temperatures, higher yields are generally obtained, reproducibility is higher, and the reactions are compatible with a wide variety of functional groups. Given all the benefits of this methodology, we set out to update the synthesis of the D_{3h} triketone **3**.

The standard conditions for palladium(0)-catalyzed coupling reactions employ a catalytic mixture of tris(dibenzylideneacetone)palladium(0) ($Pd_2(dba)_3$) and 1,1'-bis(diphenylphosphino)ferrocene (DPPF), using sodium *tert*-butoxide as a base and toluene as a solvent, all under an inert atmosphere. We tailored these conditions to the coupling of methyl anthranilate and methyl 2-iodobenzoate by exchanging DPPF for 1,4-bis(diphenylphosphino)butane (DPPB) and sodium *tert*-butoxide for sodium methoxide. By changing the ligand to DPPB, we have reduced the cost of the ligand by a fifth while maintaining the catalytic activity; not surprising since simple molecular modeling shows DPPF and DPPB to have similar binding geometries. In fact, DPPB has been used for these reactions in past but is not favored as it tends to promote β-hydride elimination when alkyl halides are used.[8-11] Since we used aryl halides exclusively, this did not affect our synthetic route. By changing the base to sodium methoxide, we eliminated the possibility of transesterification occurring while maintaining the efficacy of the coupling.

Using these conditions, we have obtained the diarylamine **1** in 80% yield however, subsequent coupling failed to give the desired triarylamine **2** (Figure 5). Despite trying multiple catalysts, ligands, bases, and solvents, we were unable to obtain this product. Interestingly though, when potassium bis(trimethylsilyl)amide was employed as the base, an unusual intramolecular cyclization occurred to give **5** in ~10% yield. It is possible that this product is being formed through a C-H activation by palladium at the sp^3-carbon of the methyl ester. Such activation at a sp^3-center is extremely unusual[12-15] and is certainly noteworthy.

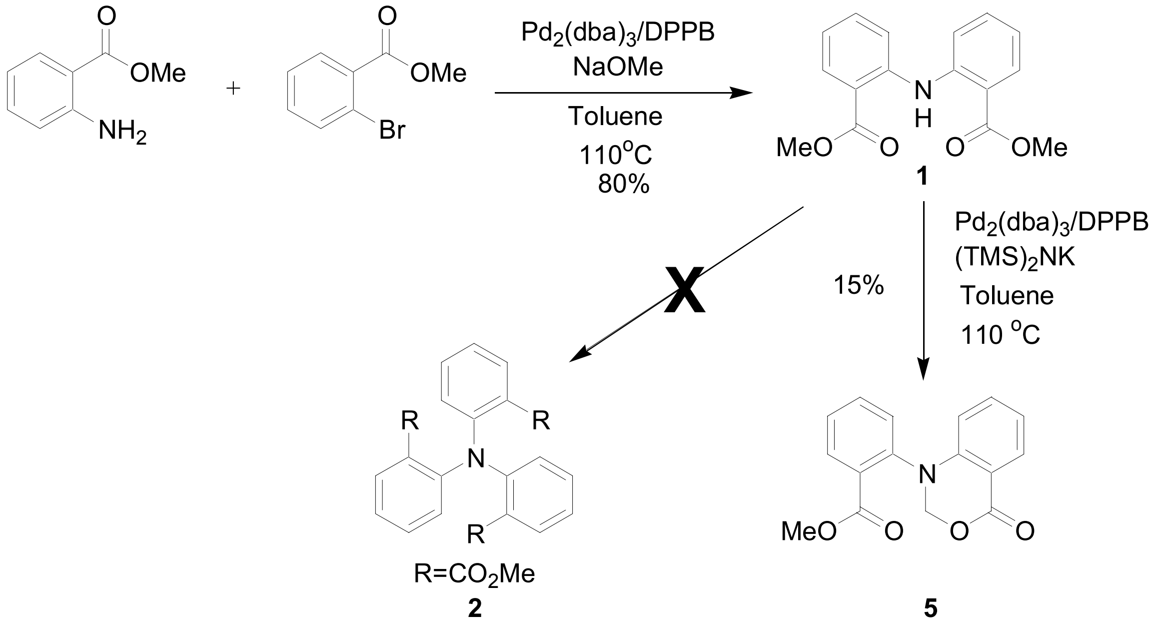


Figure 5. Synthetic procedure employing palladium(0) catalyst and the resulting intramolecular cyclization.

With the failure of palladium to achieve the desired triarylamine, we decided to see if we could synthesize the desired tri-*ortho*-ester (or acid) through lithiation chemistry (Figure 6). Tris(*p*-tolyl)amine was brominated to form tris(2-bromo-4-methylphenyl)amine **6** in 95% yield. Transmetallation with *n*-butyllithium followed by treatment with chloroethylformate gave the mono-cyclized acridone **7** in 46% yield, with no formation of the desired tri-carboxylated product. We attempted the reaction with dimethylcarbonate, carbon dioxide, and also using a zinc stabilized tri-anion, all without success.

When the above mentioned lithiated species was quenched with paraformaldehyde, we obtained the tri-*ortho*-benzylalcohol **8** in 79% yield. Oxidation using manganese dioxide gave the analogous tri-ortho-aldehyde **9** in 84% yield, however, subsequent oxidation to the desired tri-*ortho*-acid was not attained, even with strong oxidizing agents such as potassium permanganate.

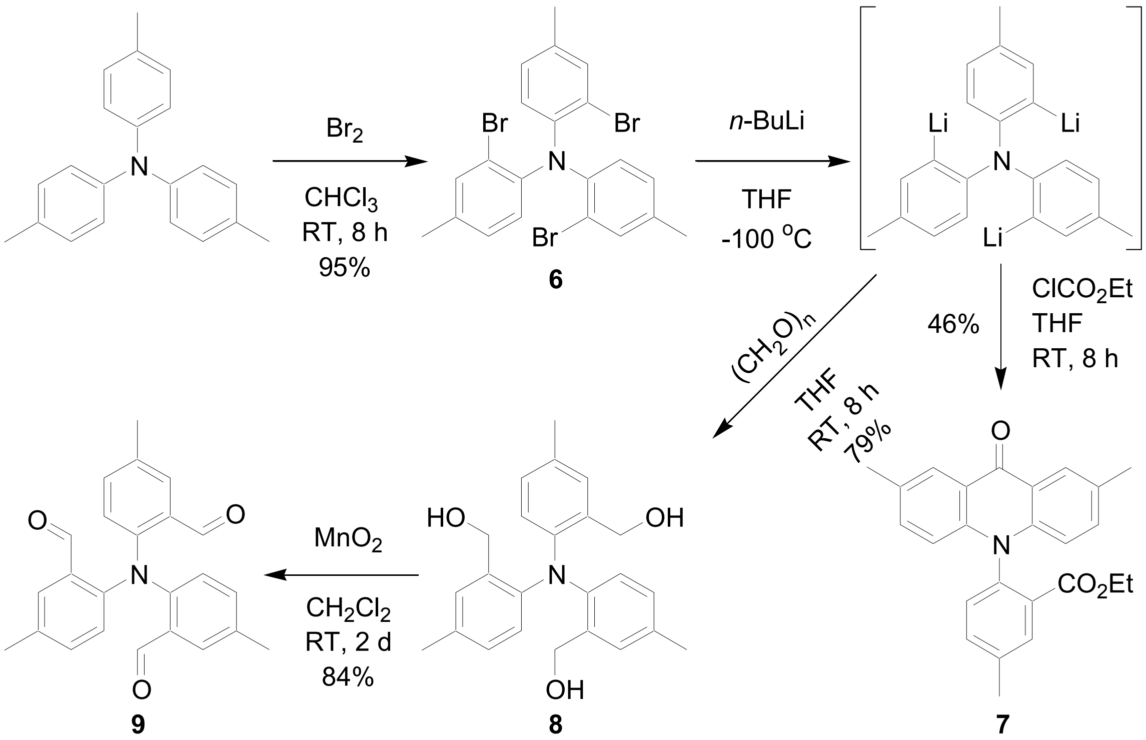


Figure 6. Synthetic procedures employing lithiation techniques.

With the failure of both palladium and lithiation chemistry to achieve the desired tri-*ortho*-functionalized triarylamine, we were forced to return to copper catalysts. Due to the many problems associated with the Ullmann-type coupling, our research group pursued the development of a soluble copper catalyst that could potentially succeed where palladium failed. The first of these catalysts developed was Cu(PPh$_3$)$_3$Br, which in combination with cesium carbonate in toluene, was able to carry out the coupling of methyl anthranilate and methyl 2-bromobenzoate to give **1** in a similar yield (83%) to palladium (Figure 7). The subsequent coupling to achieve the tri-*ortho*-functionalized triarylamine **2** required the use of a high boiling solvent, *o*-dichlorobenzene, which lead to the isolation of **2** in 40% yield.[16] Later, we showed that the Fréchet[17] modification of the Ullmann coupling could give **2** in 55% yield and in a single step; a modest improvement over the 33% obtained in the two step procedure using our copper catalyst.[16] The triarylamine **2** could then be easily converted to its analogous tri-*ortho*-acid **6** in almost quantitative yield using a standard base hydrolysis.

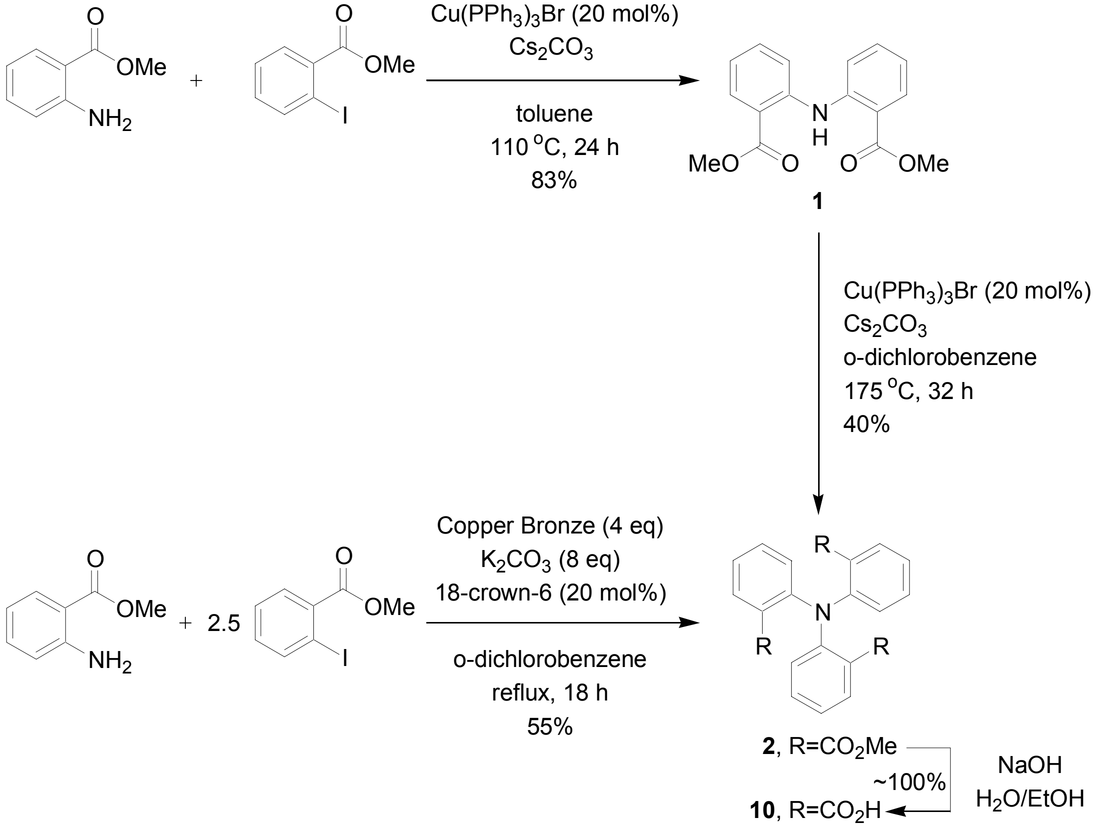


Figure 7. Synthetic procedure employing palladium(0) catalyst and the resulting intramolecular cyclization.

The Friedel-Crafts cyclization reaction that was previously carried out in boiling sulfuric acid resulted in low yields of **3**.[7] Furthermore, these harsh conditions would likely not be amiable to the functionalized derivatives that we would eventually need for the development of the higher dimensional network building blocks. It was for this reason that we developed a new, mild cyclization procedure that requires the conversion of the tri-*ortho*-acid **10** to its analogous acid chloride, followed by the *in situ* Lewis acid-catalyzed cyclization with iron(III) chloride. The reactions are carried out in refluxing dichloromethane (bp = 40 °C), giving the D_{3h} triketone **3** in 50% yield (Figure 8). Overall, this modified procedure gives the D_{3h} triketone **3** in 28% yield over three steps as compared to the previously reported 6.6% yield.

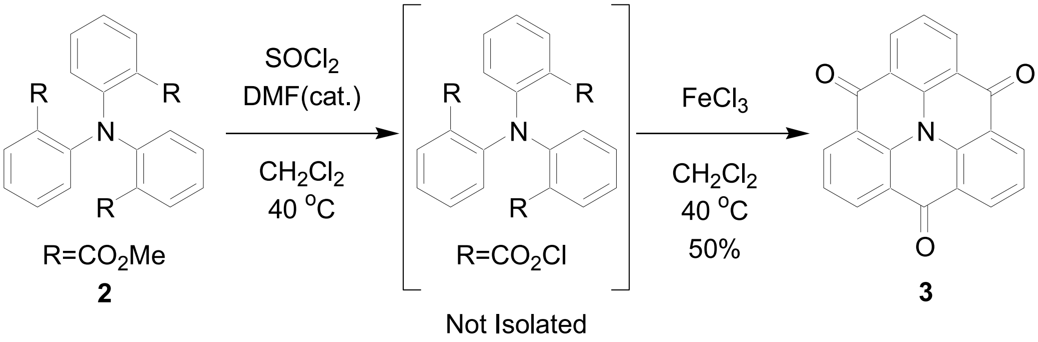


Figure 8. Modified Friedel-Crafts cyclization.

2.3 Solid State Structure:

Although the D_{3h} triketone **3** was previously synthesized,[7] there is little known about its solid state structure and properties.[18-20] In fact, prior to our work, it was debated as to whether this molecule would be planar or buckled. We found that **3** is insoluble in most common organic solvents however, we were able to grow fine crystals from boiling nitrobenzene. Single-crystal X-ray diffraction clearly shows that these molecules are indeed planar and form densely packed (Kitaigorodskii packing coefficient = 0.72) π-stacks along the *a*-axis (Figure 9). The π-stacking interactions are at a distance of 3.46 Å and are offset at an angle of 21.1°. The stacks adopt a herringbone-type structure with an angle of 26.9° between the planes of the molecules. This type of packing motif is similar to many molecular-based conductors, such as perylene.[21] The three-fold symmetry and planarity of **3** make it an ideal conjugated, electroactive building block for higher dimensional networks and discotic liquid-crystalline phases.[22]

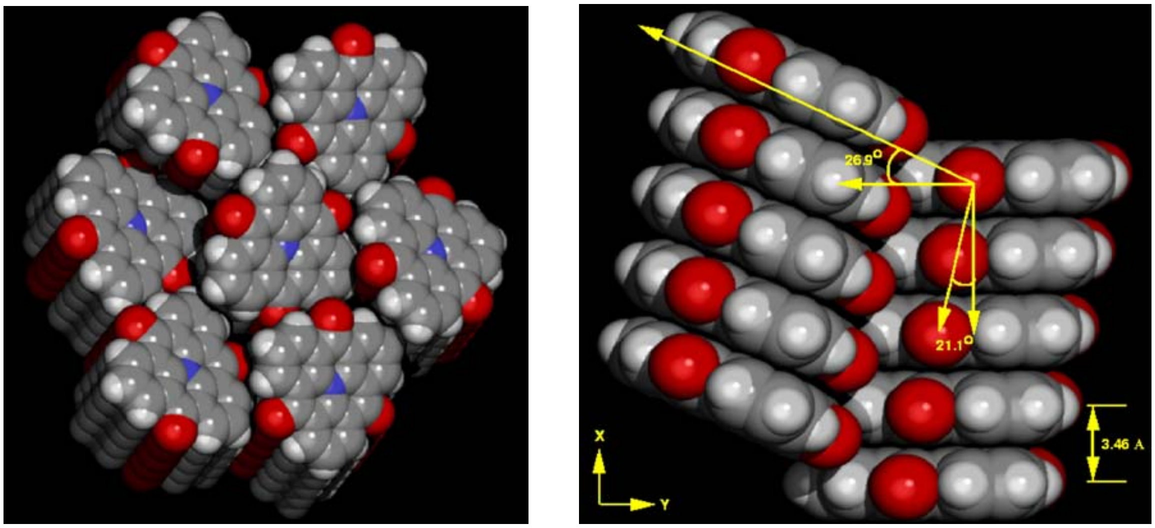


Figure 9. The packing motif (left) and stacking interactions (right) of the D_{3h} triketone **3** from single-crystal X-ray diffraction.

2.4 Photophysical and Electrochemical Properties:

The photochemical properties of the D_{3h} triketone **3** were studied along with phenylacridone (PHA) and the di-bridged triarylamine **4** for comparison. Since **3** has limited solubility in common organic solvents, the absorption and emission spectra (Figure 10) were collected using samples dissolved in 10% trifluoroacetic acid (TFA) in dichloromethane. The absorption maxima (λ_{max}) of **3**, **4**, and PHA are 422, 458, and 412 nm, respectively. When excited at these wavelengths, **3**, **4**, and PHA emit at 499 nm (green), 540 nm (yellow), and 471 nm (blue). The red shift in the emission of **4** from PHA can be attributed to the increased conjugation in the chromophore; however, this argument fails to explain the lack of a further red shift in the emission of **3**. This phenomenon may be attributed to differential protonation or an electronic transition from lower lying orbitals.[23] The quantum yield of **4** (λ_{max} = 435 nm) was measured to be 0.42 in benzene with reference to perylene (λ_{max} = 440 nm).

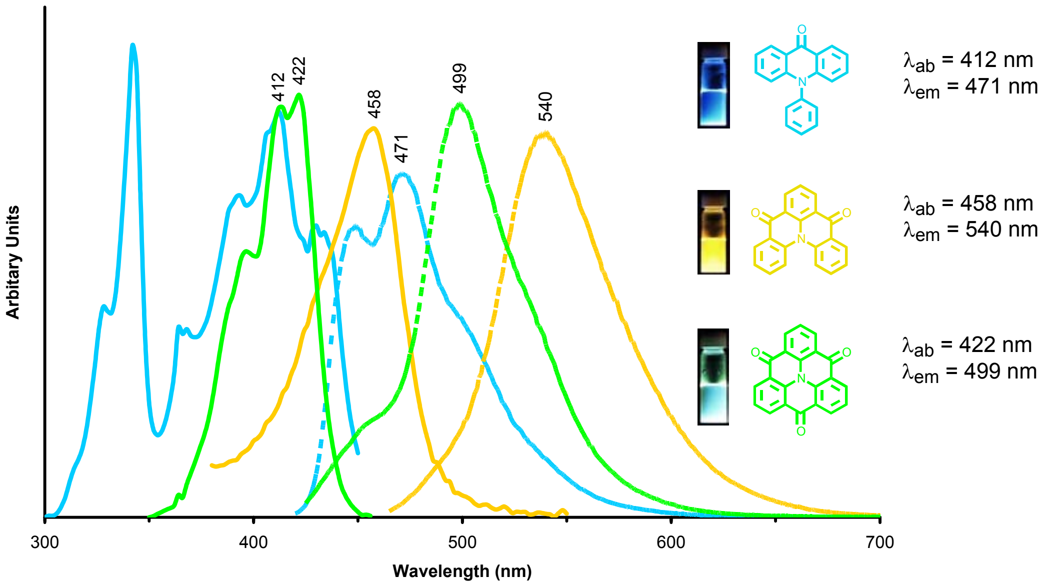


Figure 10. The absorption (solid) and emission (dashed) spectra of **3** (green), **4** (yellow), and PHA (blue). Inset pictures are photographs of these compounds (10^{-3} M in 10% TFA/CH_2Cl_2) exposed to 365 nm light.

Since the spectra were collected in an acidic medium, they are likely to correspond to a protonated or partially protonated state. It has been hypothesized that such a protonation occurs at the carbonyl oxygen rather than the heterocyclic nitrogen.[24,25] By comparing the spectral data to that of **4** and PHA in dichloromethane without TFA (Figure 11), the effect of protonation appears to be a red shift in the range of 18-20 nm for absorption and 47-69 nm for emission. Also, there appears to be a significant increase in the Stokes shift due to protonation. For example, **4** and PHA have Stokes shifts of 30 and 33 nm respectively, however, in the presence of TFA, these shifts increase to 59 and 82 nm respectively. This effect could be due to a large difference between the excited and ground state conformations of the protonated species.

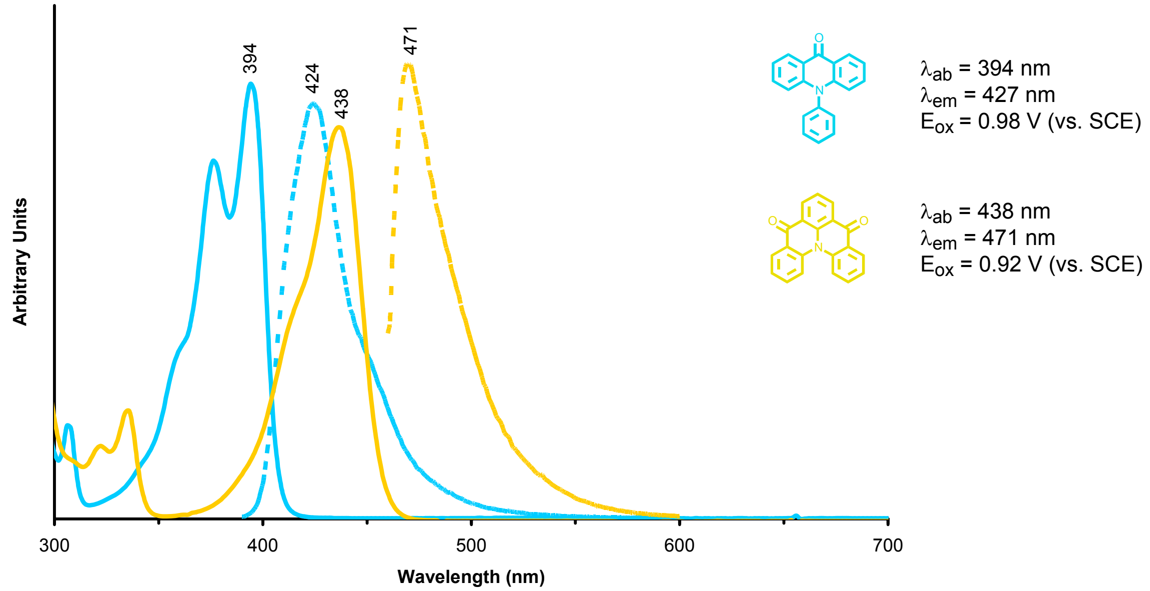


Figure 11. The absorption (solid) and emission (dashed) spectra of **4** (yellow) and PHA (blue) as 10^{-3} M solutions in CH_2Cl_2 without TFA. The oxidation potentials from cyclic voltammetry are also given.

Cyclic voltammetry of **4** and PHA show irreversible oxidation potentials (vs SCE) at 0.92 and 0.98 V as compared to that of triphenylamine at 1.01 V.[26] The oxidation potential of **3** was not obtained due to its low solubility in suitable organic solvents.

2.5 Conclusion:

We have developed a new approach for the synthesis of the D_{3h} triketone **3** that is a significant improvement over the original methodology, both in the yield and the mildness of the conditions. Furthermore, the inability of palladium catalysts to couple *ortho*-substituted aryl amines and aryl halides has inspired the development of a series of new copper catalysts. The mild conditions of the new synthetic procedure will increase the tolerance to various functional groups which will be required for the construction of higher dimensional electronic solids. The photochemical spectra show that **3** and **4** are highly luminescent conjugated chromophores. The structure of **3**, obtained by single-crystal X-ray diffraction, clearly illustrates the planarity of this molecule and it's ability to form columnar π-stacks, making it an ideal building block for 3- and (3, *n*)-connected networks and discotic phases.[27, 28]

The major challenge facing the future of this research lies in the functionalization of the D_{3h} triketone **3**. This is made especially difficult by the insolubility of this compound in common organic solvents. One possible solution would be to functionalize the molecule prior to cyclization; this would be facilitated by the mild conditions of the new cyclization methodology. Even simple functional groups may be able to significantly disrupt the π-stacking interactions of these planar systems and thus increase the solubility. One can even envisage functionalizing the positions *para* to the nitrogen with long-chain alkyl groups for the assembly of discotic phases.[29] Another possibility is to change the oxygen atoms to sulfur to induce a sulfur-sulfur interaction between the columnar π-stacks and thus reduce the angle of the herringbone interaction from 26.9° to 0°. Such a system would be three-dimensional and may have very interesting conduction properties.

2.6 References:

(1) Hoffmann, R.; Janiak, C.; Kollmar, C. "A Chemical Approach to the Orbitals of Organic Polymers" *Macromolecules* **1991**, *24*, 3725-3746.

(2) Conwell, E. M. "The Differences between One-Dimensional and 3-Dimensional Semiconductors" *Phys. Today* **1985**, *38*, 46-53.

(3) Wegner, G. "Polymers with Metal-Link Conductivity-Preview of their Synthesis, Structure and Properties" *Angew. Chem. Int. Ed.* **1981**, *20*, 361-381.

(4) Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. "New triarylamine-containing polymers as hole transport materials in organic light-emitting diodes: Effect of polymer structure and cross-linking on device characteristics" *Chem. Mater.* **1998**, *10*, 1668-1676.

(5) Shirota, Y. "Organic materials for electronic and optoelectronic devices" *J. Mater. Chem.* **2000**, *10*, 1-25.

(6) Weck, M.; Dunn, A. R.; Matsumoto, K.; Coates, G. W.; Lobkovsky, E. B.; Grubbs, R. H. "Influence of perfluoroarene-arene interactions on the phase behavior of liquid crystalline and polymeric materials" *Angew. Chem. Int. Ed.* **1999**, *38*, 2741-2745.

(7) Hellwinkel, D.; Melan, M. "Heteropolycyclic compounds of the triangulene type. I. 8,12-Dihydro-4H-benzo[1,9]quinolizino[3,4,5,6,7-difg]acridine-4,8,12-trione and 5,9-dihydroquino[3,2,1-de]acridine-5,9-dione" *Chem. Ber.* **1971**, *104*, 1001-1016.

(8) Hartwig, J. F. "Carbon-heteroatom bond-forming reductive eliminations of amines, ethers, and sulfides" *Acc. Chem. Res.* **1998**, *31*, 852-860.

(9) Hartwig, J. F. "Transition metal catalyzed synthesis of arylamines and aryl ethers from aryl halides and triflates: Scope and mechanism" *Angew. Chem. Int. Ed.* **1998**, *37*, 2047-2067.

(10) Muci, A. R.; Buchwald, S. L. "Practical palladium catalysts for C-N and C-O bond formation",*Cross-Coupling Reactions, Vol. 219*, **2002**; pp 131-209.

(11) Yang, B. H.; Buchwald, S. L. "Palladium-catalyzed amination of aryl halides and sulfonates" *J. Organomet. Chem.* **1999**, *576*, 125-146.

(12) Zucca, A.; Cinellu, M. A.; Pinna, M. V.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. "Cyclopalladation of 6-substituted-2,2 '-bipyridines. Metalation of unactivated methyl groups vs aromatic C-H activation" *Organometallics* **2000**, *19*, 4295-4304.

(13) Dyker, G. "Palladium-Catalyzed C-H Activation of Methoxy Groups - a Facile Synthesis of Substituted 6h-Dibenzo B,D Pyrans" *Angew. Chem. Int. Ed.* **1992**, *31*, 1023-1025.

(14) Dyker, G. "Transition-Metal-Catalyzed Annelation Reactions .5. Palladium-Catalyzed C-H Activation of Tert-Butyl Groups - a Simple Synthesis of 1,2-Dihydrocyclobutabenzene Derivatives" *Angew. Chem. Int. Ed.* **1994**, *33*, 103-105.

(15) Catellani, M.; Motti, E.; Ghelli, S. "Intramolecular benzylic C-H activation: palladium-catalyzed synthesis of hexahydromethanofluorenes" *Chem. Commun.* **2000**, 2003-2004.

(16) Gujadhur, R.; Venkataraman, D.; Kintigh, J. T. "Formation of aryl-nitrogen bonds using a soluble copper(I) catalyst" *Tetrahedron Lett.* **2001**, *42*, 4791-4793.

(17) Gauthier, S.; Frechet, J. M. J. "Phase-Transfer Catalysis in the Ullmann Synthesis of Substituted Triphenylamines" *Synthesis* **1987**, 383-385.

(18) Hellwinkel, D.; Aulmich, G.; Melan, M. "Modified tetrahelicene systems" *Chem. Ber.* **1976**, *109*, 2770-2784.

(19) Hellwinkel, D.; Melan, M. "Heteropolycycles of the triangulene type. II. Stereochemistry of bridged triarylamines" *Chem. Ber.* **1974**, *107*, 616-626.

(20) Hellwinkel, D.; Schmidt, W. "Modified tetrahelicene systems. III. Doubly ortho-bridged triphenylamine derivatives" *Chem. Ber.* **1980**, *113*, 358-384.

(21) Almeida, M. H., R. T. "Handbook of Organic Conductive Molecules and Polymers*" Handbook of Organic Conductive Molecules and Polymers Vol. 1*; Nalwa, H. S.; John Wiley & Sons: New York, **1997**, 87-149.

(22) Nelson, J. "Solar energy - Solar cells by self-assembly?" *Science* **2001**, *293*, 1059-1060.

(23) Semiempirical calculations (ZINDO/S) of the electronic spectra using the program Hyperchem show a similar trend to that observed experimentally.

(24) Nuckolls, C.; Katz, T. J.; Castellanos, L. "Aggregation of conjugated helical molecules" *J. Am. Chem. Soc.* **1996**, *118*, 3767-3768.

(25) Kawata, H.; Niizuma, S. "Acid-Base-Equilibrium in Excited-State of 10-Methylacridone" *J. Prakt. Chem.-Chem. Ztg.* **1994**, *336*, 425-428.

(26) Faber, R.; Mielke, G. F.; Rapta, P.; Stasko, A.; Nuyken, O. "Anodic oxidation of novel hole-transporting materials derived from tetraarylbenzidines. Electrochemical and spectroscopic characterization" *Collect. Czech. Chem. Commun.* **2000**, *65*, 1403-1418.

(27) Bushey, M. L.; Hwang, A.; Stephens, P. W.; Nuckolls, C. "Enforced stacking in crowded arenes" *J. Am. Chem. Soc.* **2001**, *123*, 8157-8158.

(28) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. "Functionalized pentacene: Improved electronic properties from control of solid-state order" *J. Am. Chem. Soc.* **2001**, *123*, 9482-9483.

(29) Schmidt-Mende, L.; Fechtenkotter, A.; Mullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. "Self-organized discotic liquid crystals for high-efficiency organic photovoltaics" *Science* **2001**, *293*, 1119-1122.

CHAPTER 3

BRIDGED TRIARYLAMINES – A NEW CLASS OF HETEROHELICENES

3.1 Introduction:

Since the pioneering work by Newman and Lednicer in 1955 on hexahelicene,[1,2] there have been numerous carbo- and heterohelicenes developed in order to exploit the unique properties of these inherently helical molecules.[3-6] A few potential applications of these compounds include asymmetric molecular recognition,[7-9] nonlinear optics,[10] liquid crystals,[11] and circularly polarized luminescence (CPL)[12] for back-lighting in LCD displays.[13-16]

Helicenes are inherently chiral molecules and have been designated the symbols (+) or *P* (for plus) and (-) or *M* (for minus) to describe the two possible helical twists (Figure 12). These designations are often referred to as right-handed or left-handed helicity, respectively. One can determine this configuration by curling the fingers of the appropriate hand in the direction of the helical coil, while the thumb points in the direction of the ascending helix.

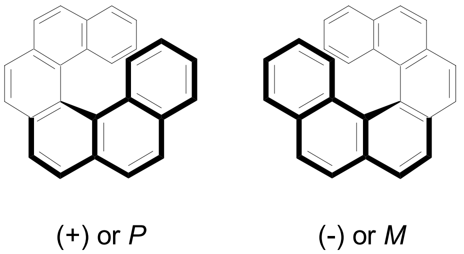


Figure 12. The absolute configurations of hexahelicene.

Within the class of heterohelicenes, there are three major subdivisions: oxahelicenes,[3,17] thiahelicenes,[18,19] and azahelicenes[20,21] which correspond to helicenes containing the heteroatoms oxygen, sulfur, and nitrogen respectively (Figure 13). The synthesis of all of these systems is relatively difficult, usually requiring photochemical or radical reactions which result in low yields and multiple side products.[3, 17, 22-25] The synthesis of functionalized helicenes is even more difficult and has thus inhibited the exploration of these systems as functional materials. Recently, Katz and co-workers reported a new, high-yielding synthesis of functionalized carbohelicenes that does not require radical or photocyclization.[26] This work represents a milestone for helicenes as a viable source for interesting functional materials.

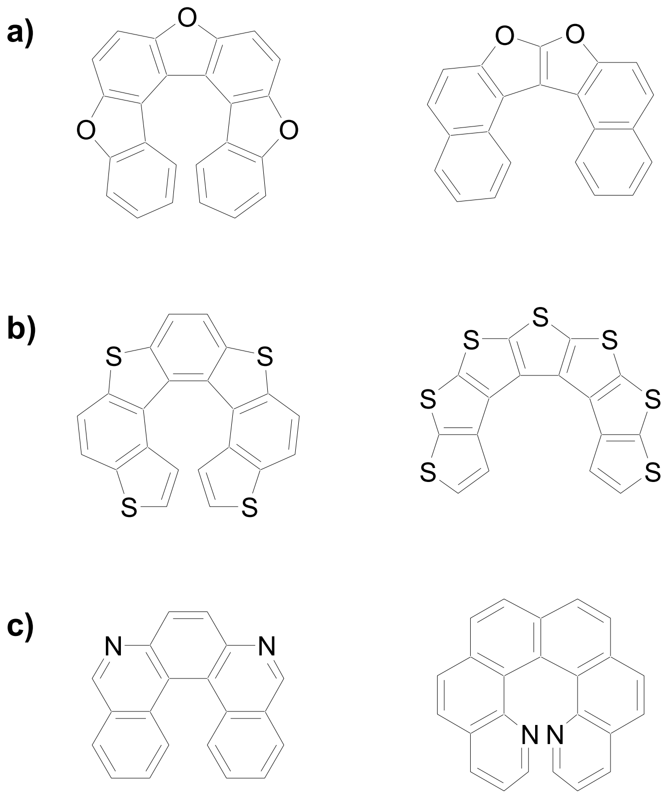


Figure 13. Representative molecules of the three major types of heterohelicenes: a) oxahelicenes, b) thiahelicenes, and c) azahelicenes.

Despite the popularity of helicenes and their many potential applications, there has been little effort devoted to the design of an electroactive heterohelicene in which the heteroatom can be oxidized to a radical cation. Such a helicene would allow further study into how molecular helicity effects bulk electronic properties such as charge transport and conductance.[27] As a first step towards this goal, we set out to synthesize a series of heterohelicenes based on triarylamine, a moiety that has been widely exploited in hole-transport materials for organic light emitting diodes (OLEDs) due to its electronic, photochemical, and physical properties.[28]

3.2 Synthesis:

In Chapter 2, we discussed the properties of the bridged triarylamine **4**, which was first synthesized by Hellwinkel and Melan[29,30] and later by our research group.[31] Although this compound proved to be a highly luminescent chromophore, cyclic voltammetry showed that its oxidation was irreversible in nature. This observation is not surprising since the chemical transformations of unfunctionalized triarylamines upon oxidation are very well documented.[32,33] For example, triphenylamine forms an unstable monocation radical at ~0.98 V, which rapidly dimerizes to form tetraphenylbenzidine (Figure 14). In order to stabilize the radical cation, substituents can be introduced at the *para* position(s) of the triarylamine. Tris(4-bromophenyl)amine is very stable upon oxidation and even (4-methoxyphenyl)-diphenylamine has been described as quite stable.[32] Therefore, it was desirable for us to make a substituted bridged triarylamine in order to improve the stability of the radical cation.

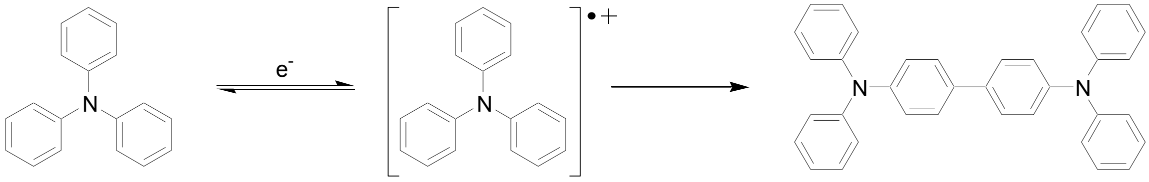


Figure 14. The oxidation and subsequent dimerization of triphenylamine to tetraphenylbenzidine.

The simplest route to a substituted bridged triarylamine is through lithiation chemistry such as that described for compound **7** in Chapter 2, Figure 6, followed by cyclization. Although this route is efficient, it has several major drawbacks. First, the lithiation chemistry is limited to functional groups that are not base sensitive. This may pose a problem if this procedure is to be widely applicable to future bridged triarylamine derivatives. Also, this strategy is limited to triphenylamines. Larger aryl groups like naphthalene, which could extend the helical overlap of the molecule, would brominate in a position not conducive to cyclization. Thus, we would be unable to synthesis larger heterohelicenes by this route.

An alternative strategy involves the synthesis of an *ortho*-functionalized triarylamine followed by cyclization. To this end, we coupled *p*-toluidine with two equivalents of methyl 2-iodobenzoate to make the functionalized triarylamine **11** in 70% yield (Figure 15). Subsequent hydrolysis and cyclization gave a 1:1 mixture of the symmetric (**12**) and unsymmetric (**13**) isomers which were inseparable by chromatography. The formation of this unsymmetric isomer is not only problematic for isolation and purification, but for synthetic efficiency as well. If a synthetic strategy could be devised that only allowed the symmetric heterohelicene to be formed, we could in theory double our product yield.

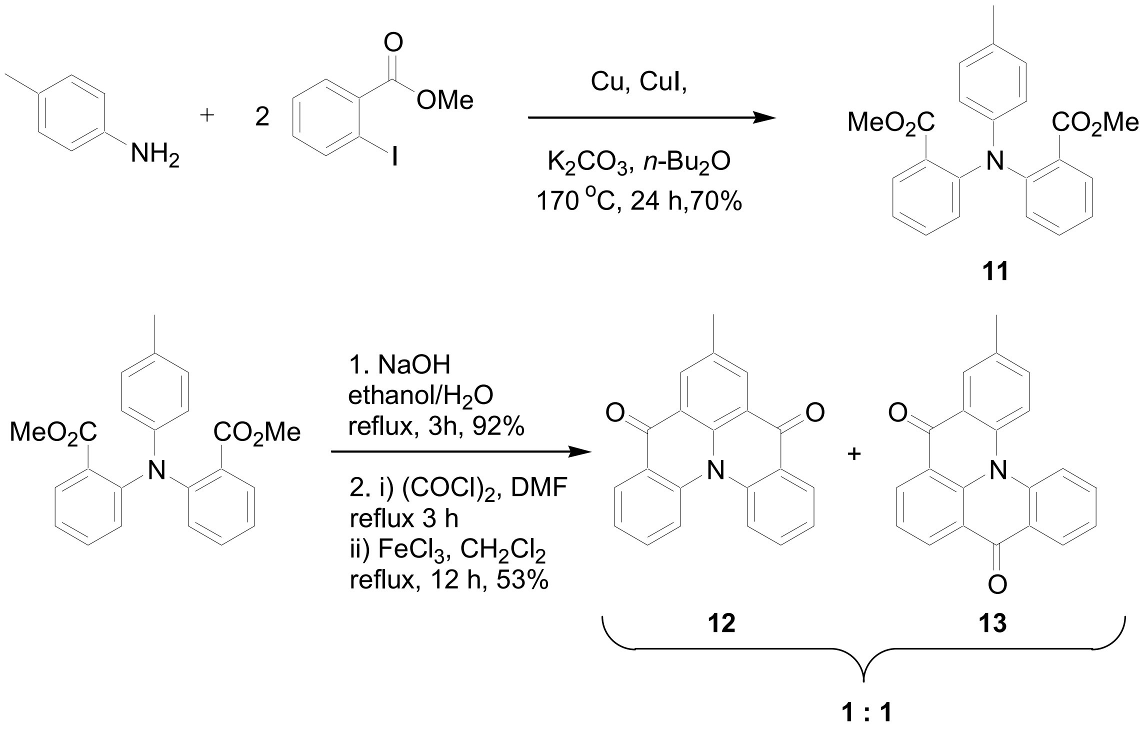


Figure 15. The synthesis of mixed symmetric and unsymmetric di-bridged triarylamines.

To solve this problem, we devised a strategy to synthesize a triarylamine in which the two carboxyl moieties to be cyclized would be on the same ring (Figure 16), thus ensuring only one mode of cyclization that of the desired symmetric heterohelicene. There are two major drawbacks to this strategy, first, the functionalized aryl bromide must first be synthesized and second, the added steric bulk of two *ortho*-esters may hinder the coupling reaction.

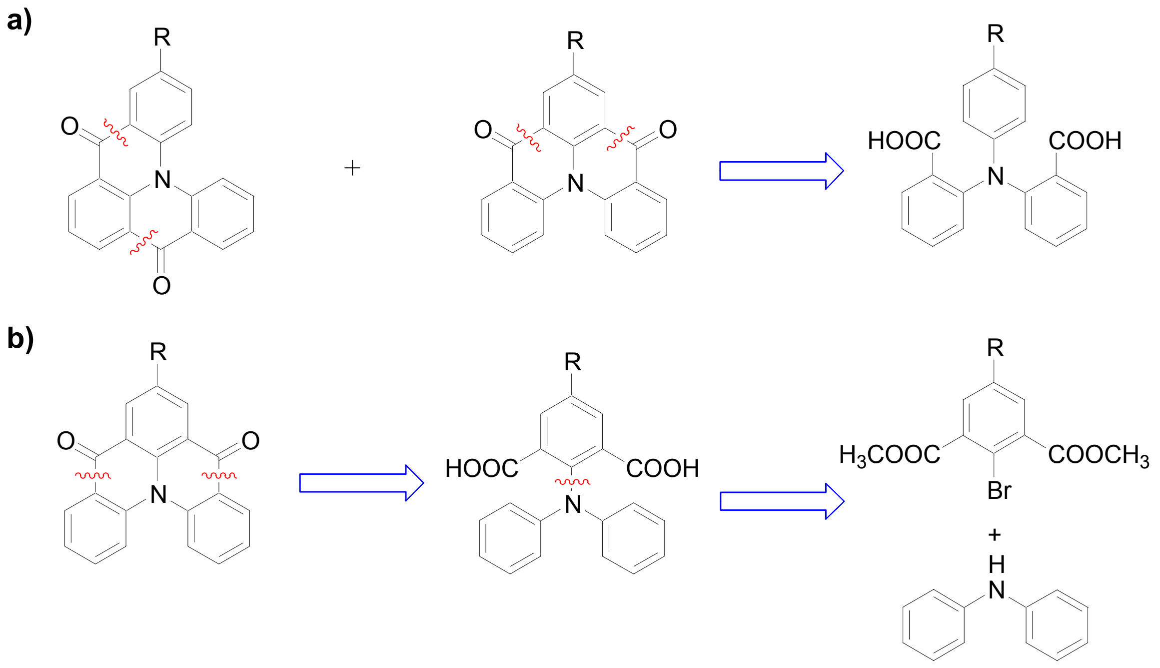
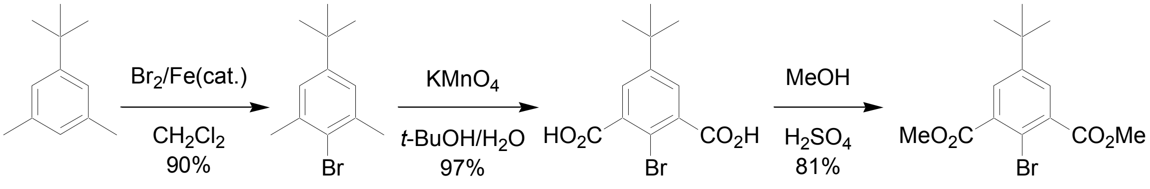


Figure 16. The synthetic strategies for bridged triarylamines: a) the original strategy leading to a mixture of symmetric and unsymmetric isomers and b) the new strategy with the carboxyl groups on the same ring, leading exclusively to the symmetric product.

The synthesis of the *tert*-butylbromodiester **16** was achieved in three simple chemical transformations from the affordable and commercially available 5-*tert*-butyl-*m*-xylene (Figure 17).[34-36] The bromination was carried out in chloroform with a catalytic amount of iron powder, giving the brominated product **14** in 90% after re-crystallization from ethanol. This product was then oxidized with potassium permanganate in a *tert*-butanol/water solution, giving the *tert*-butylbromodiacid **15** in 97% yield. Finally, the diacid **15** was esterified in methanol and concentrated sulfuric acid to give the final product **16** in 81% yield after re-crystallization from hexane. The overall yield of this simple three-step synthesis is 71%. Furthermore, these reactions are amenable to scale-up and do not require any purification from chromatographic techniques.



14 **15** **16**

Figure 17. The high yielding three-step synthesis of the *tert*-butylbromodiester **16**.

We initially attempted to couple **16** to diphenylamine using the palladium-catalyzed reactions reported by Hartwig[37,38] and Buchwald[39,40] but we were unable to obtain the desired product using these methodologies. The coupling of **16** to diphenylamine was eventually obtained using the copper-catalyzed Ullmann conditions (Figure 18). The yield (85%) of **17** was remarkably high considering the bulky reactants. We hypothesize that although the *ortho*-esters introduce some steric interference, the carbon-bromine bond becomes activated by the electron-withdrawing effect of these substituents. Subsequent hydrolysis gave the diacid of **17** in 97% yield. We carried out the cyclization using oxalyl chloride and tin(IV) chloride, which gave the desired heterohelicene **18** in 80% yield. It should be noted that cyclization using thionyl chloride and iron(III) chloride caused chlorination of the product at the open positions *para* to the central nitrogen to give **19**.

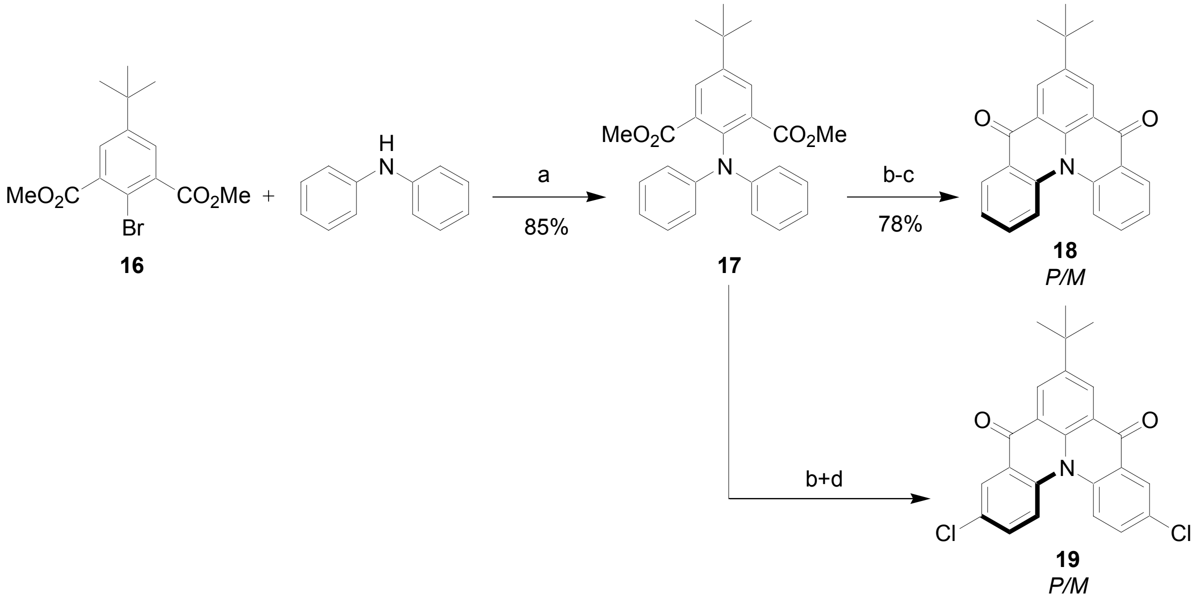


Figure 18. The synthesis of the bridged triarylamine **18**. Reaction Conditions: a) Copper bronze (15 mol%), K_2CO_3 (1.2 eq), Ph_2O, 190 °C, 48 h. b) NaOH (20 eq), EtOH/H_2O (1:1), reflux, 12 h. c) i) oxalyl chloride (2.2 eq), CH_2Cl_2, reflux, 30 min. ii) $SnCl_4$ (2.2 eq), reflux, 3 h. d) i) $SOCl_2$, reflux, 3 h. ii) $FeCl_3$ (4.0 eq), CH_2Cl_2, reflux, 18 h.

It is not until the size of the diarylamine is increased that we see a significant reduction in the yield of the Ullmann coupling, presumably due to steric interference introduced on the nucleophile. N-phenyl-1-naphthylamine was coupled to **16** to give **20** in 63% yield using the same conditions as for **17** (Figure 19). Subsequent hydrolysis gave the diacid in 95% yield, which was then cyclized to give the second heterohelicene **21** in 78% yield.

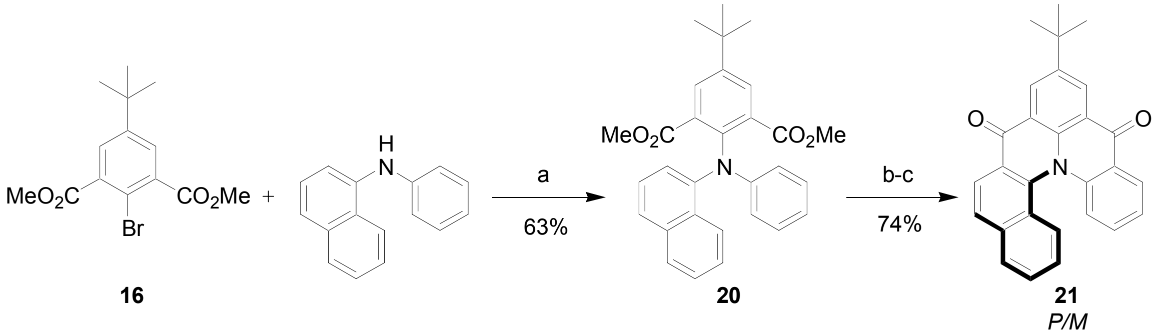
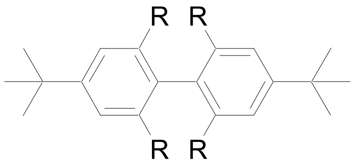
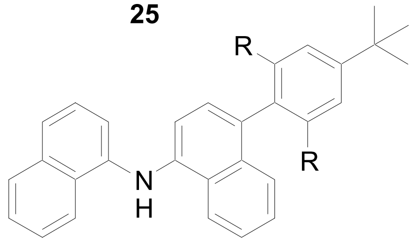


Figure 19. The synthesis of the bridged triarylamine **21**. Reaction Conditions: a) Copper bronze (15 mol%), K_2CO_3 (1.2 eq), Ph_2O, 190 °C, 96 h. b) NaOH (20 eq), EtOH/H_2O (1:1), reflux, 12 h. c) i) oxalyl chloride (2.2 eq), CH_2Cl_2, reflux, 30 min. ii) $SnCl_4$ (2.2 eq), reflux, 3 h.

The next molecule in the series of heterohelicenes was more difficult to synthesize as the starting dinaphthylamine **22** is not commercially available. However, this compound can be easily synthesized in 89% yield using palladium-catalyzed chemistry (Figure 20). This dinaphthylamine oxidizes rapidly and must therefore be stored under argon and at -40 °C after purification. The dinaphthylamine can be coupled to **16** using a stoichiometric amount of copper(I) iodide in di-*n*-butylether to give **23** in 24% yield. This low yield is not only attributed to the increased steric bulk of the dinaphthylamine, but also by competitive reactions that lead to the dimer of the aryl halide **25** and the coupled product **26**. Subsequent hydrolysis of **23** gave the diacid in 95% yield which was then cyclization to give the third heterohelicene **24** in 60% yield.



25



26

R=CO_2Me

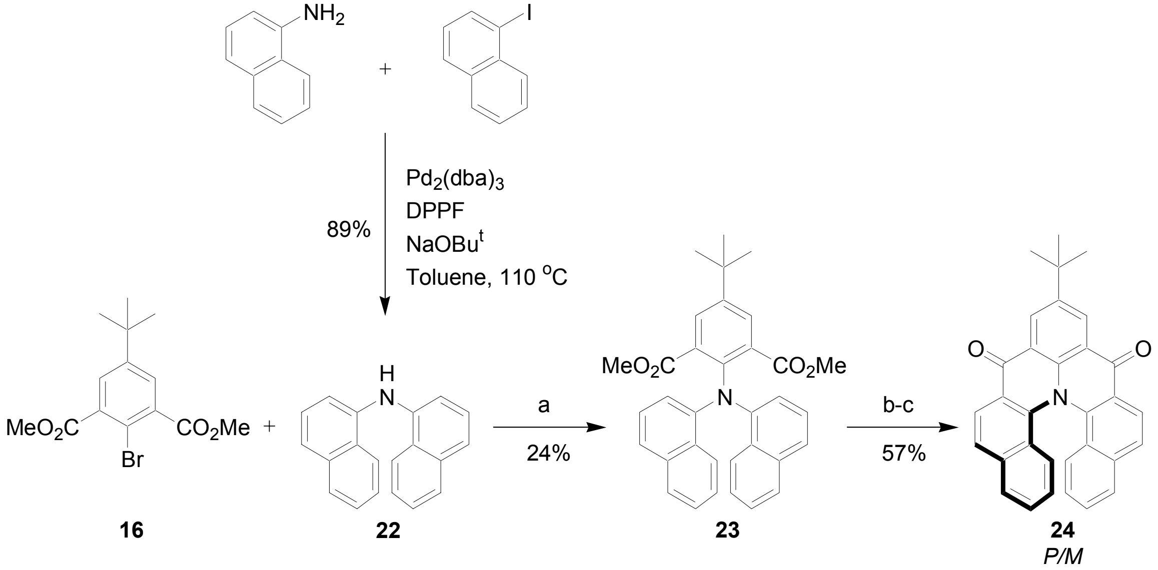


Figure 20. The synthesis of the bridged triarylamine **24**. Reaction Conditions: a) Copper(I) iodide (1.0 eq), K_2CO_3 (2.0 eq), *n*Bu_2O, 150 °C, 120 h. b) NaOH (20 eq), EtOH/H_2O (1:1), reflux, 72 h. c) i) oxalyl chloride (2.5 eq), CH_2Cl_2, reflux, 30 min. ii) $SnCl_4$ (2.5 eq), reflux, 3 h.

To summarize, we have developed a simple three-step procedure for the synthesis of a series of heterohelicenes based on bridged triarylamines (Figure 21). Furthermore, this synthesis provides one of the simplest routes to a helicene of any kind, and does not require any photochemistry or radical cyclization reactions. The starting materials are simple to make, amenable to scale-up, and easily purified. Also, the *tert*-butylbromodiester **16** is modular in nature and can simply be coupled to the appropriate diarylamine in order to obtain any of the three heterohelicenes. The overall yields of the heterohelicenes **18**, **21**, and **24** by this three-step procedure are 66, 47, and 14%, respectively.

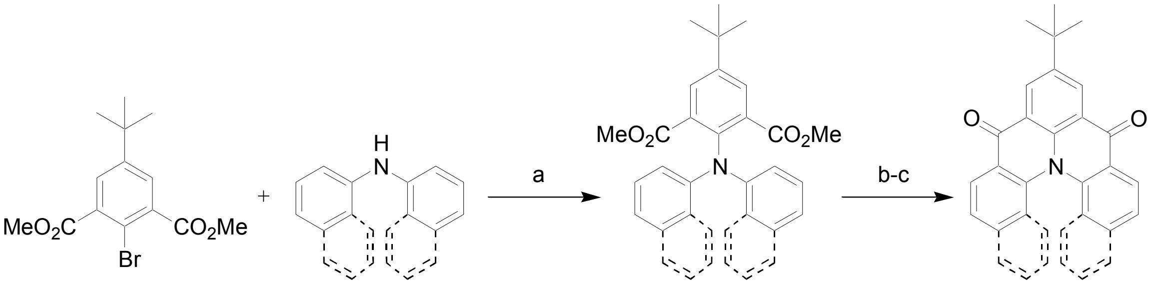


Figure 21. The three-step synthesis of bridged triarylamine heterohelicenes. Reaction Conditions: a) Cu or CuI, K_2CO_3, Ph_2O or $n$$Bu_2O$, 150-190 °C, 48-120 h. b) NaOH, EtOH/H_2O (1:1), reflux, 12-72 h. c) i) oxalyl chloride, CH_2Cl_2, reflux, 30 min. ii) $SnCl_4$, reflux, 3 h.

3.3 Solid State Structure:

The increasing helical overlap of the aromatic rings in molecules **18**, **21**, and **24** can be observed as a shielding effect in the proton nuclear magnetic resonance (NMR) spectra (Figure 22). The result is a characteristic upfield shift of proton “e” in molecules **18** to **21**. Similarly, the chemical shifts of protons “g'/g” and “f'/f” are also shifted upfield from molecules **21** to **24**. Such a shielding effect by the increasingly overlapping aromatic rings is a common phenomenon observed in carbohelicenes.[3]

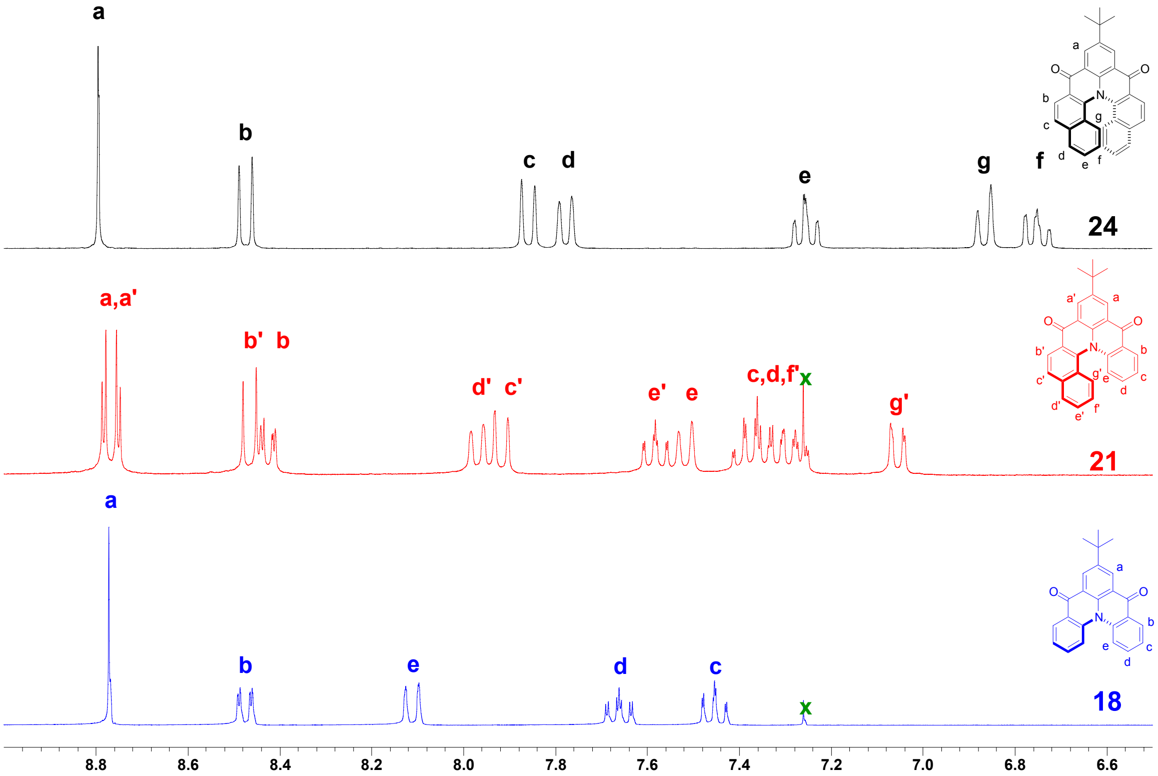


Figure 22. Aromatic region of the 300 MHz ^{1}H-NMR spectra of racemic **18** (blue), **21** (red), and **24** (black). The $CDCl_3$ solvent peaks are denoted by "x" (green).

Single crystal X-ray diffraction of **18**, **21**, and **24** shows that the helical twist of these compounds is indeed sterically driven by the increasing overlap of the terminal aryl rings (Figure 23). Looking at the packing motif (Figure 24), it can be seen these molecules exist as racemic mixtures of atropisomers which π-stack in a ziz-zag motif, similar to that observed in hydrogen-bonded *ortho*-substituted diphenylamines.[41] This is yet another example of helically biased molecules which prefer to adopt the zig-zag supramolecular structure over a helical one, at least when present as a racemic mixture. The interplanar angle (θ) between the terminal rings of **18**, **21**, and **24** are 43.4°, 58.8°, and 60.1° respectively. In comparison, this angle is 58.5° in hexahelicene and ~70° in binaphthyl. The slope (ϕ) of the zig-zag in **18**, **21**, and **24** is 21.6°, 79.0°, and 61.0°. The repeat distances (d_1) for **18**, **21**, and **24** are 12.0 Å, 14.5 Å, and 14.1 Å with the distance between atropisomers (d_2) being 6.0 Å, 4.7 Å, and 7.1 Å. It should be noted that for **21**, the d_2 is not half of d_1, which denotes a dimeric-type stacking in which terminal phenyl-phenyl and naphthyl-naphthyl π-interactions preferentially form between the unsymmetrical atropisomers.

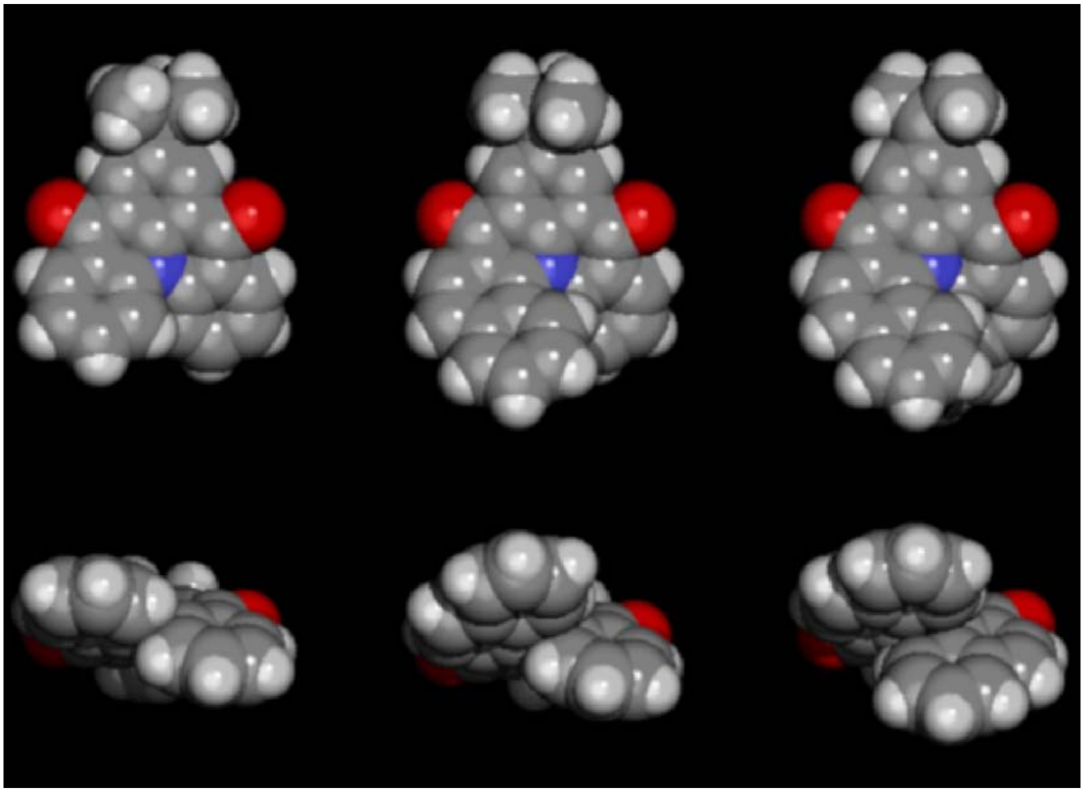
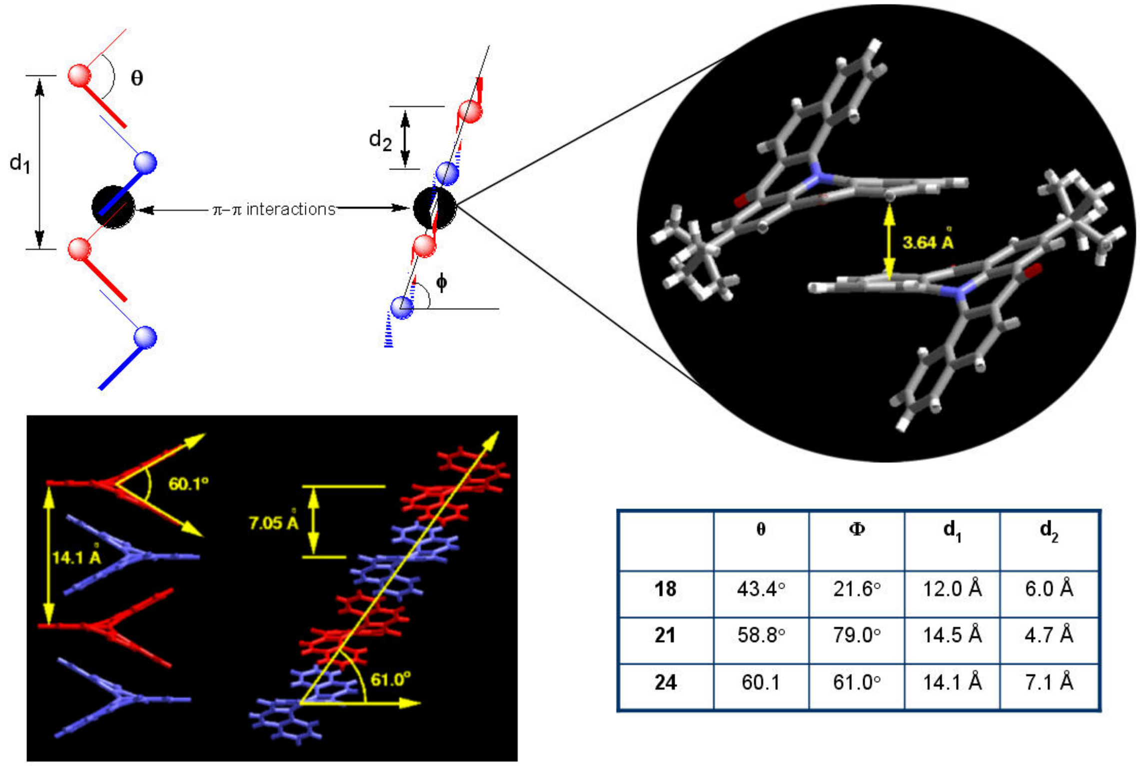


Figure 23. Space-filling renderings from the single crystal X-ray diffraction data of **18**, **21**, and **24** (from left to right) as viewed from above (top) and side (bottom). Only a single atropisomer is shown.



	θ	Φ	d_1	d_2
18	43.4°	21.6°	12.0 Å	6.0 Å
21	58.8°	79.0°	14.5 Å	4.7 Å
24	60.1	61.0°	14.1 Å	7.1 Å

Figure 24. Schematic of the ziz-zag packing motif observed in **18**, **21**, and **24** (top left) as seen from the side and rotated 90°. The analogous image from the single crystal X-ray diffraction of **24** is shown (bottom left) with the π-stacking interactions magnified (top right). *P*-isomers (blue) and *M*-isomers (red) are shown with the methyl groups of the *tert*-butyl moiety removed for clarity. A summary of the packing distances and angles is given as a table (bottom right).

3.4 Chemical Reactivity:

The reactivity of **18** to halogenation is the same as that observed in triarylamines, namely the positions *para* to the nitrogen are the most susceptible to electrophilic aromatic substitution. This is illustrated by the formation of **19** when thionyl chloride and iron(III) chloride are used for the cyclization. Furthermore, the mono-bromination of **21** to give **27** illustrates that the portion of the helicene that is extended with a naphthyl moiety is more susceptible to attack by bromine (Figure 25).

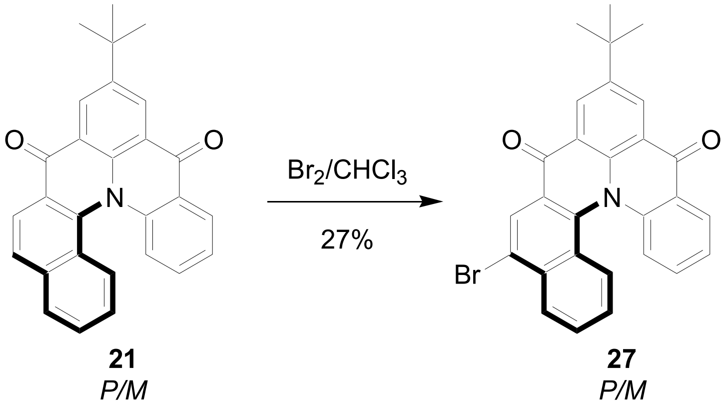


Figure 25. Preferential bromination of **21** at the naphthyl moiety to give **27**.

Interestingly, when **24** was treated with benzyltrimethylammonium tribromide (BTMABr$_3$) and calcium carbonate in a methanol solution, product **28** was isolated in a 75% yield (Figure 26). We believe that this reaction proceeds through a bromonium ion intermediate which is then attacked by the nucleophilic methoxide anion.

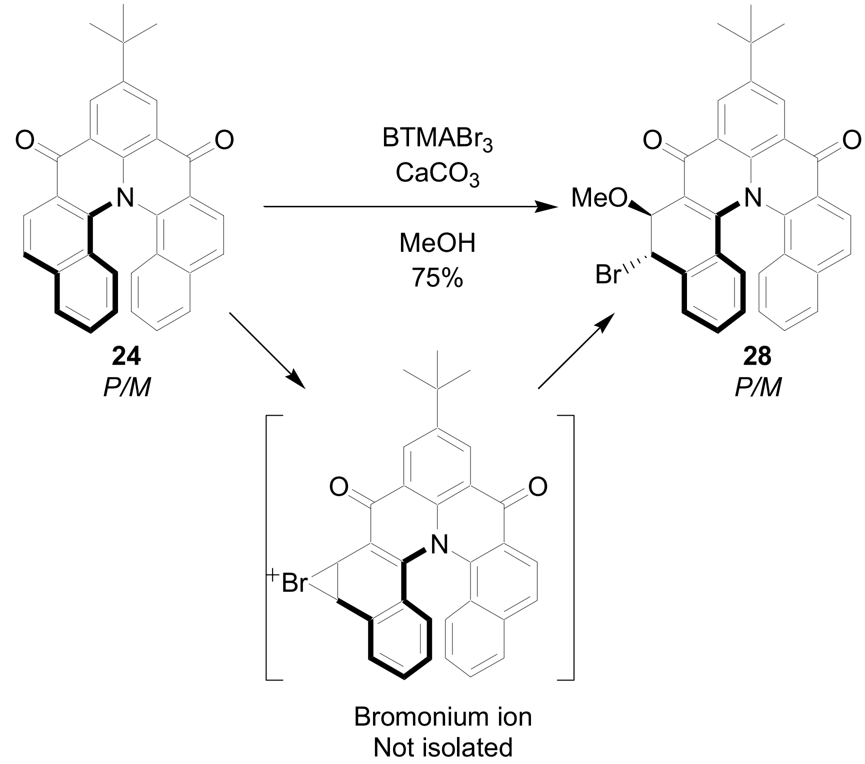


Figure 26. Alkene-like bromination of **24** at the naphthyl moiety to give **28**.

This type of reactivity is common in phenanthrene, hexahelicene, and other fused polyaromatic systems due to partial bond fixation, in which one of the double bonds of an aromatic ring reacts like an isolated alkene due to resonance.[42] This case is particularly interesting in that there is only a single naphthyl group, thus, there is a substantial loss of energy when one ring loses its aromaticity. The increased double bond character at this position can be explained through the additional resonance contributions by the nitrogen center and the carbonyl bridge (Figure 27). Thus, **24** has four of five resonance structures that contribute to the isolation of the reactive double bond, the same as that observed in phenanthrene. It should be noted that there are other resonance contributors to the overall structure of **24**, however, only the ones that affect the region of the localized double bond are shown.

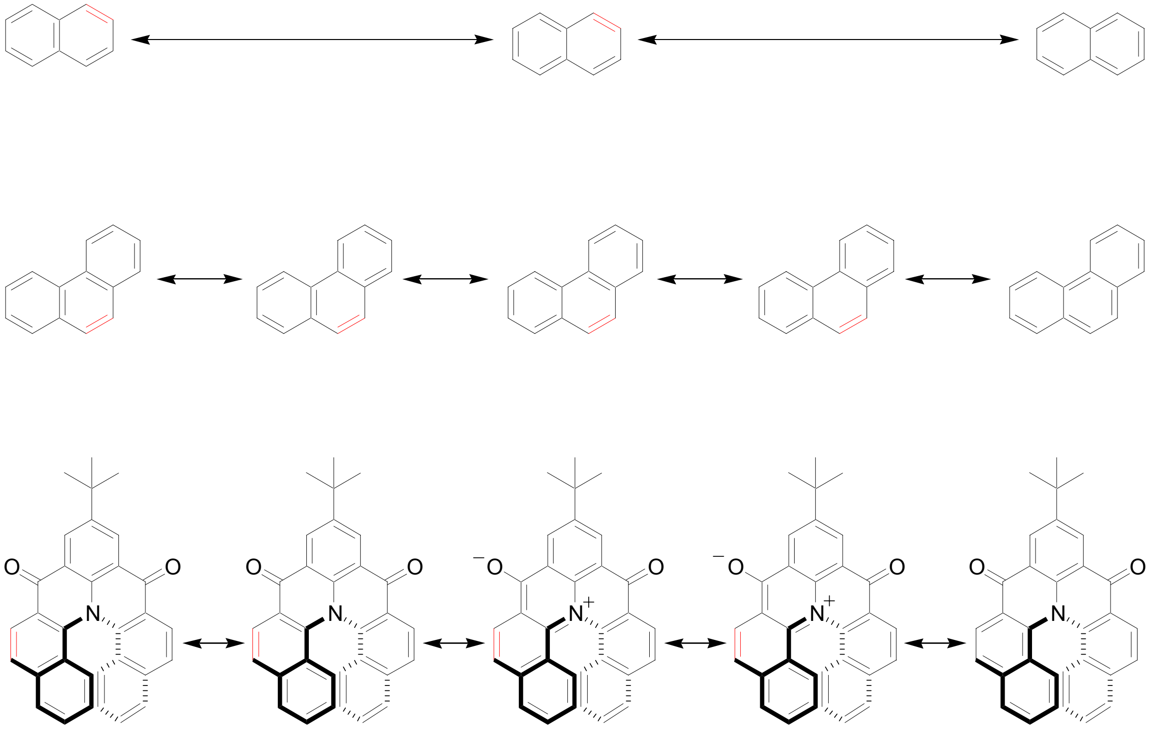


Figure 27. Resonance contributions to the partial bond fixation observed in naphthalene, phenanthrene, and **24**. The bonds with the highest double-bond character are shown in red.

3.5 Photophysical Properties:

The absorption and emission spectra (Figure 28) of these molecules were obtained from chloroform solutions at concentrations of 2 × 10^{-5} M and ~1 × 10^{-6} M, respectively. The absorption maxima (λ_{max}) of **18**, **21**, and **24** are 442, 446, and 460 nm, with extinction coefficients (ε) of 22.6 × 10^3, 17.7 × 10^3, and 14.4 × 10^3 cm^{-1} M^{-1}, respectively. These absorption maxima are much higher than those observed for carbo- and thiahelicenes of the same size.[3] When excited at these wavelengths, **18**, **21**, and **24** emit at 460, 468, and 486 nm. The observed red shift in the absorption and emission spectra are consistent with increasing conjugation of the chromophore. It is interesting to note that the absorption maximum of **24** coincides with the emission maximum of **18**, suggesting that energy transfer between these molecules may be possible.

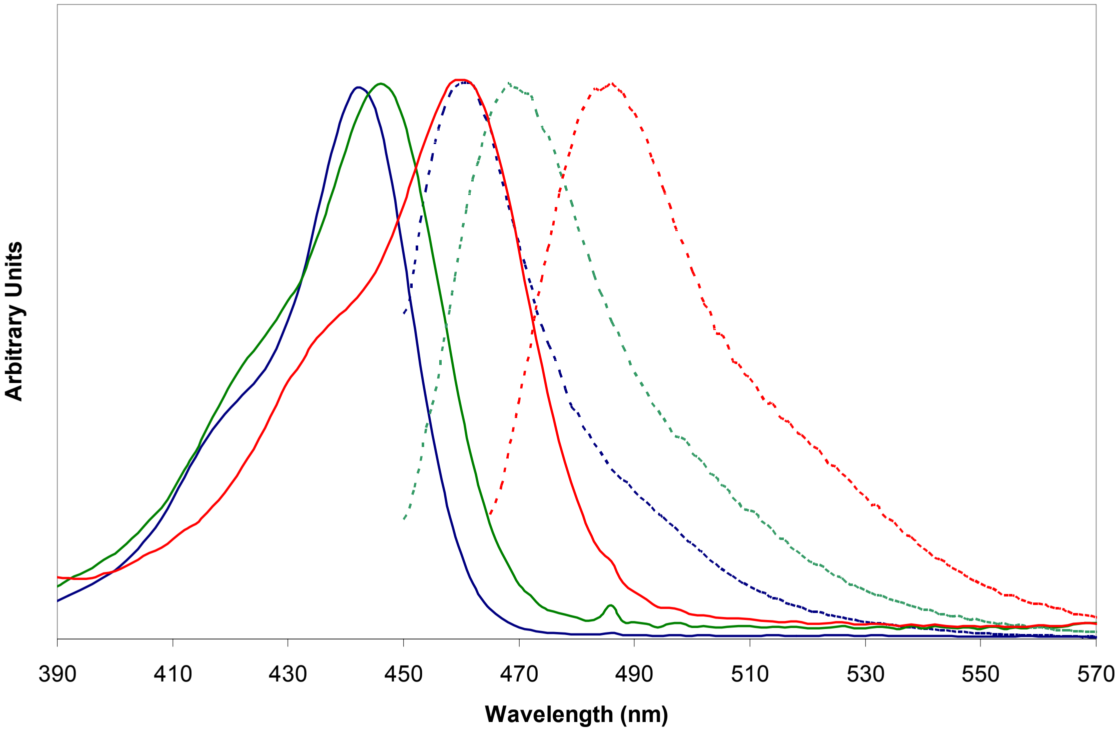


FIGURE 28. Absorption (solid) spectra of 2 × 10^{-5} M and emission (dashed) spectra of ~1 × 10^{-6} M solutions of **18** (blue), **21** (green), and **24** (red) in $CHCl_3$. All spectra were normalized to the same peak intensity for ease of viewing.

3.6 Electrochemical Properties:

Cyclic voltammetry of **18**, **21**, and **24** was conducted in dichloromethane solutions at concentrations of 1 × 10^{-3} M (Figure 29). Compound **18** shows a quasi-reversible, one-electron oxidation at $E_{1/2}$ = 1.57 V (vs. SCE), which is similar to some substituted phenyl acridones.[43] Compounds **21** and **24** show oxidation potentials at $E_{1/2}$ = 1.44 V and $E_{1/2}$ = 1.49 V, respectively. In comparison, triphenylamine forms an unstable monocation radical at ~0.98 V, which rapidly dimerizes to form tetraphenylbenzidine (Figure 14).[32, 33] There is no evidence of a dimerization or any other chemical process taking place when these bridged triarylamines are oxidized. This is a good indication as to the stability of the radical cation formed upon oxidation. This stabilization may in part be attributed to the presence of the *tert*-butyl substituent which blocks the top *para* position where dimerization would be most likely to occur. Also, the carbonyl bridges may stabilize the radical cation by contributing additional resonance pathways.

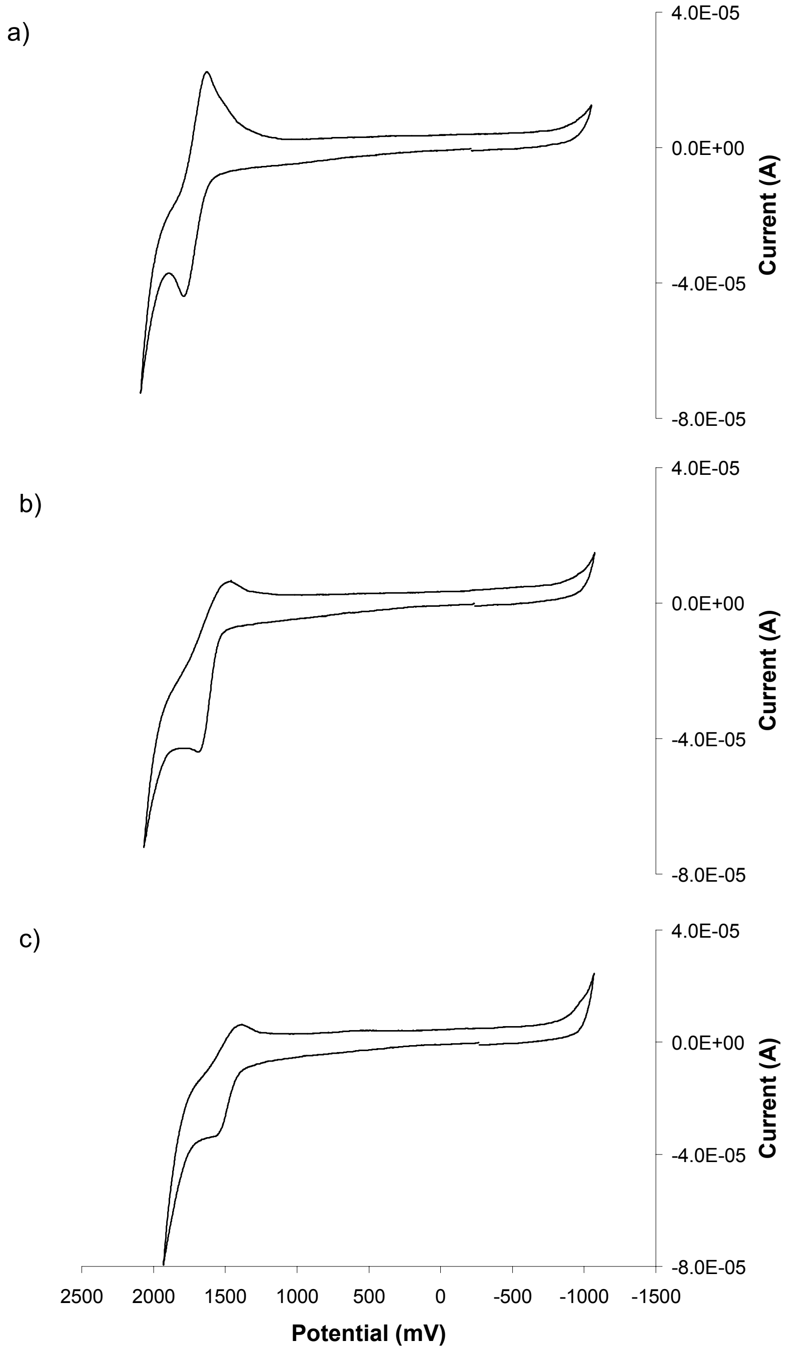


FIGURE 29. Cyclic voltammograms of a) **18**, b) **21**, and c) **24** in CH_2Cl_2.

The ESR spectra of the radical cations of the three compounds where taken as concentrated solutions in dichloromethane with an excess of antimony(V) chloride as the oxidant (Figure 30). As expected,[44] **18** shows a three line signal at 3440 G that corresponds to a single nitrogen radical with a hyperfine a_N = 7.67 G when simulated to a correlation of 0.980. **21** and **24** show a broad single line signal at 3440 G with no distinguishable hyperfine coupling.

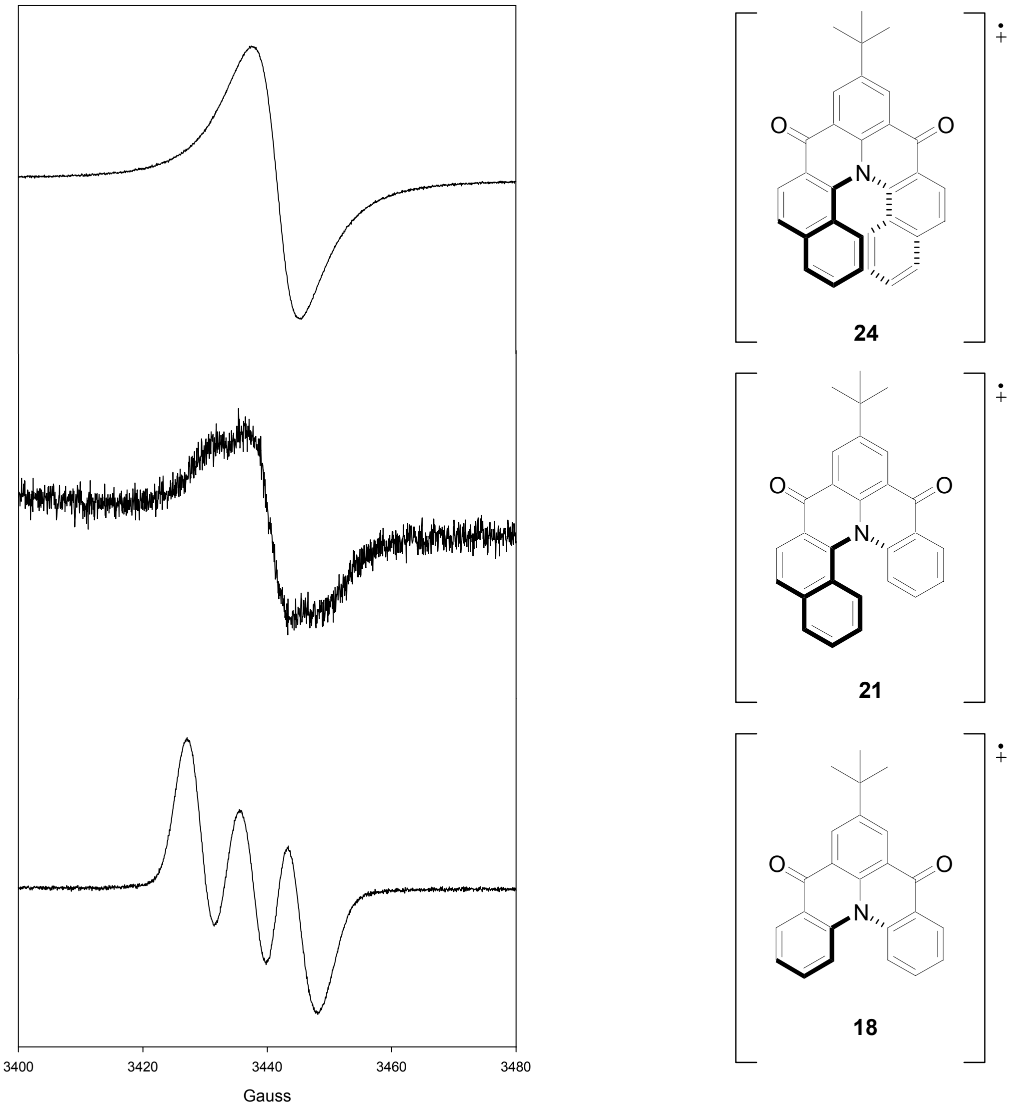


FIGURE 30. ESR spectra of the radical cations of **18**, **21**, and **24** in CH_2Cl_2 with $SbCl_5$.

3.7 Separation of Atropisomers:

Katz and coworkers have recently utilized (1*S*)-camphanates for the separation of carbohelicenes.[45] By adding this chiral substituent onto the helicene, the mixture of enantiomers becomes a mixture of diastereomers. Each of these diastereomers has unique physical properties that allows for their separation. For example, the position of the (1*S*)-camphanate with respect to an *M*-helicene favors the lactone pointing down, as opposed to up with respect to the *P*-helicene (Figure 31). Thus, the polarity of the (1*S*) camphanate substituted *P*-helicene tends to be more polar than the analogous *M*-helicene, allowing for separation of the diastereomers by simple column chromatography.

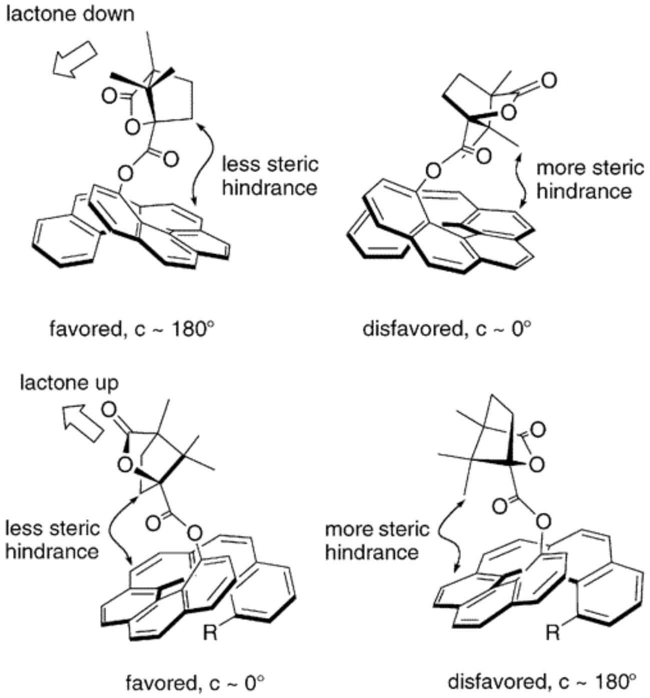


FIGURE 31.[45] Illustration of the interactions of (1*S*)-camphanate with *M*-helicene (top) and *P*-helicene (bottom) which give rise to a difference in polarity.

In order to separate their carbohelicenes, Katz and coworkers used a total of four (1*S*)-camphanate substituents on a single helicene molecule. However, if their models of the favored interactions of the camphanate and helicene are true, then a single camphanate substituent strategically placed at the innermost position of the helicene should be enough to allow for separation of the diastereomers. With this in mind, we set out to synthesize the derivatives of our bridged triarylamines substituted with a (1*S*)-camphanate.

The first step was to make a diphenylamine with an *ortho*-methoxy functionality which could later be deprotected to a phenol, to which the camphanate could be readily attached (Figure 32). Thus, aniline was coupled with 2-iodoanisole in near quantitative yields using the palladium(0)-catalyzed Hartwig[37,38]/Buchwald[39,40] type coupling. Next, the same *tert*-butylbromodiester **16** that we used in our previous helicene syntheses was coupled with **29** to give **30** in 70% yield. Subsequent hydrolysis and cyclization gave the substituted heterohelicene **31** in 80% yield. Deprotection of the methoxy group was first tried using boron tribromide but we were unable to isolate any product. The deprotection was eventually obtained by refluxing the substrate in a mixture of hydrobromic and acetic acids to give **32** in 60% yield. Finally, (1*S*)-camphanic acid chloride was reacted with **32** to give **33** as an atropdiastereomeric mixture of the *P*- and *M*- isomers in 85% yield.

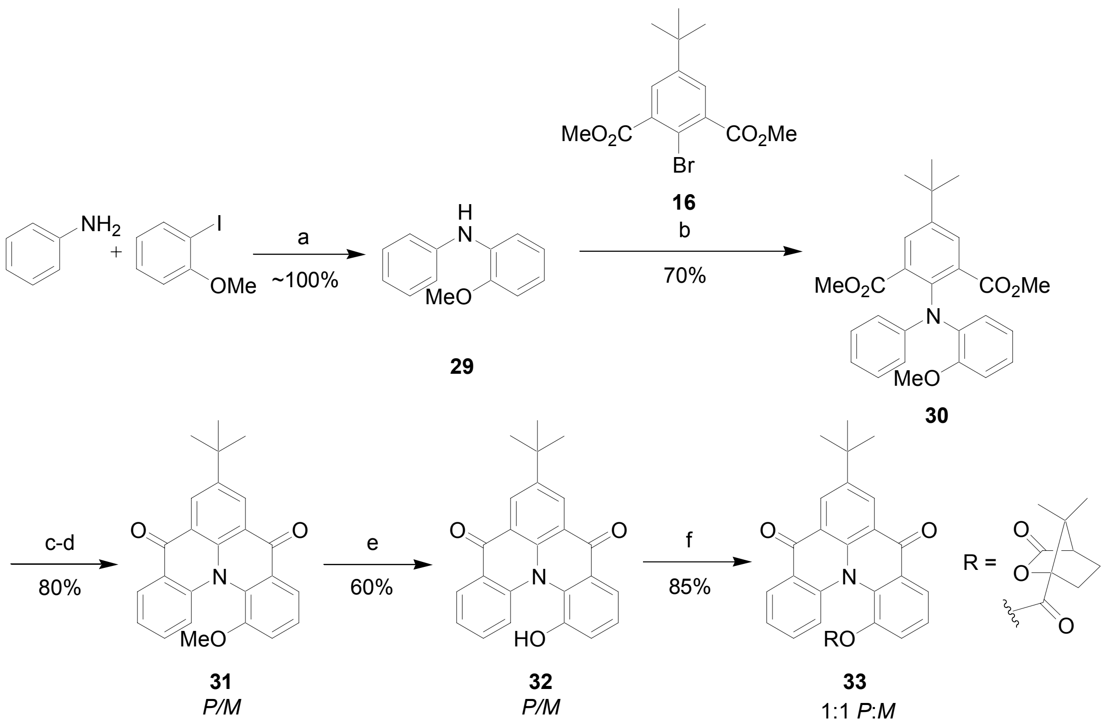


FIGURE 32. Synthesis of (1*S*)-camphanate substituted bridged triarylamine heterohelicene **33**. Reaction conditions: (a) $Pd_2(dba)_3$, DPPF, $NaOBu^t$, toluene, 110 °C; (b) Cu, CuI, K_2CO_3, $(n\text{-}Bu)_2O$, 170 °C, 3d; (c) NaOH, H_2O/EtOH (1:1), reflux then HCl; (d) $(ClCO)_2$, CH_2Cl_2, reflux 0.5 h then $SnCl_4$, reflux 2 h; (e) 1:2 AcOH:HBr, reflux, 3 d; (f) DMAP, (*S*)-Camphanic chloride, CH_2Cl_2, reflux, 12 h.

Once synthesized, the diastereomeric mixture of **33** was subjected to column chromatography using 1:1 hexane/ethyl acetate as the eluent. Two products were obtained, the first (higher R_f) was pure by NMR, however, the second product (lower R_f) showed evidence of the starting alcohol (**32**) remaining. Thus, a second column using 10:1 dichloromethane/ether as the eluent was necessary to separate the second diastereomer. A two-dimensional thin-layer chromatography (TLC) plate (Figure 33) shows the positions of the two products and the remaining alcohol relative to each other in each of the solvent mixtures.

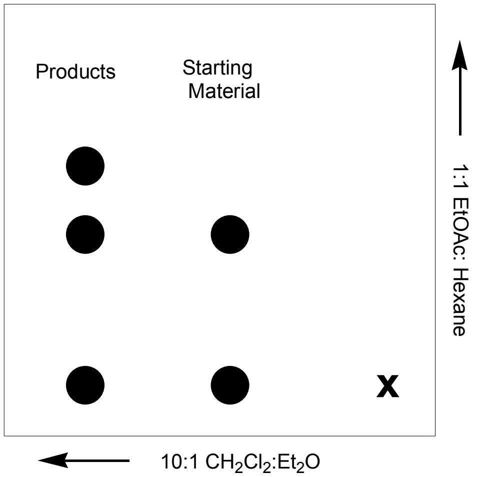


FIGURE 33. Illustration of the two-dimensional TLC plate of the reaction mixture of helicene **33**.

Assuming that the interactions described in Figure 31 are valid, it would stand to reason that the product with the higher R_f would be *M*-**33** and the product with the lower R_f would be *P*-**33**. The aliphatic regions of the ^{1}H-NMR spectra of these molecules support these assignments (Figure 34). There are three methyl groups associated with the camphanate, one adjacent to the carbonyl group (H_c) and two attached to the bridging carbon (H_a and H_b). In the ^{1}H-NMR spectra, the methyl group adjacent to the carbonyl (H_c) would be the most deshielded and thus have the highest chemical shift (~1.04 ppm). Also, from Figure 31 and 34, H_c would be the least effected by the position of the camphanate relative to the helicene and would therefore be relatively unchanged in the spectra, which agrees with our experimental observation. The remaining two methyl groups (H_a and H_b) are more affected by the configuration of the helicene. For example, in *M*-helicene, these methyl groups are pointing away from the helicene and would thus be unaffected by its ring currents. On the other hand, in the *P*-helicene, H_a is pointing towards the helicene and would thus be subjected to a shielding effect that would result in a lower chemical shift. This shielding effect is evident in the spectra as H_a is shifted from ~0.78 ppm to ~0.62 ppm in the *M*- and *P*- isomers, respectively.

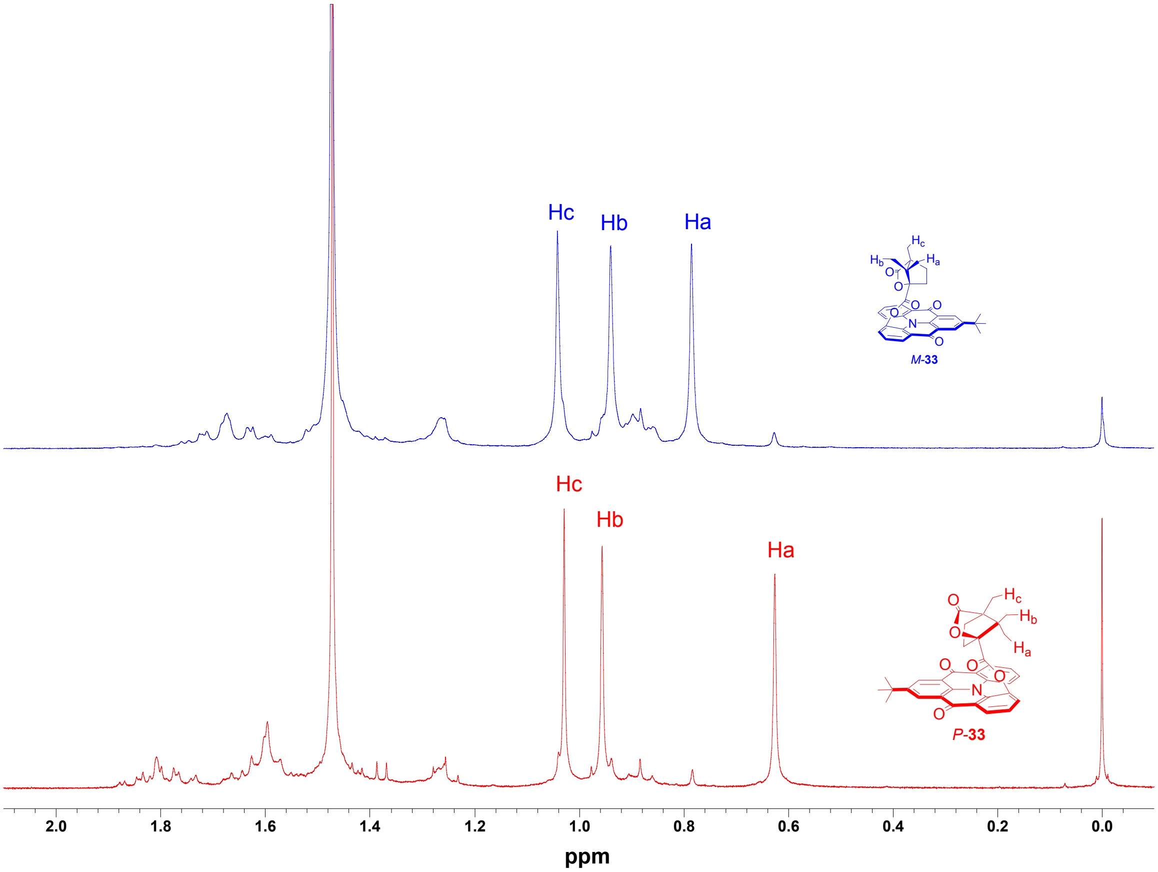


FIGURE 34. 300 MHz ^{1}H-NMR spectra of the aliphatic regions of *M*-**33** (blue) and *P*-**33** (red) in $CDCl_3$.

Definitive evidence for the separation of the diastereomers is given by the circular dichroism (CD) spectra[46-53] of the two products (Figure 35). The signals recorded are opposite in sign which is indicative of identical compounds with opposite chirality. Since the chirality of the (1*S*)-camphanate is the same on each diastereomer, the difference in the signs of the spectra must be arising from the helicene. This would make sense since the helicene is a strong chromophore and would be expected to exhibit stronger absorption characteristics than the camphanate.

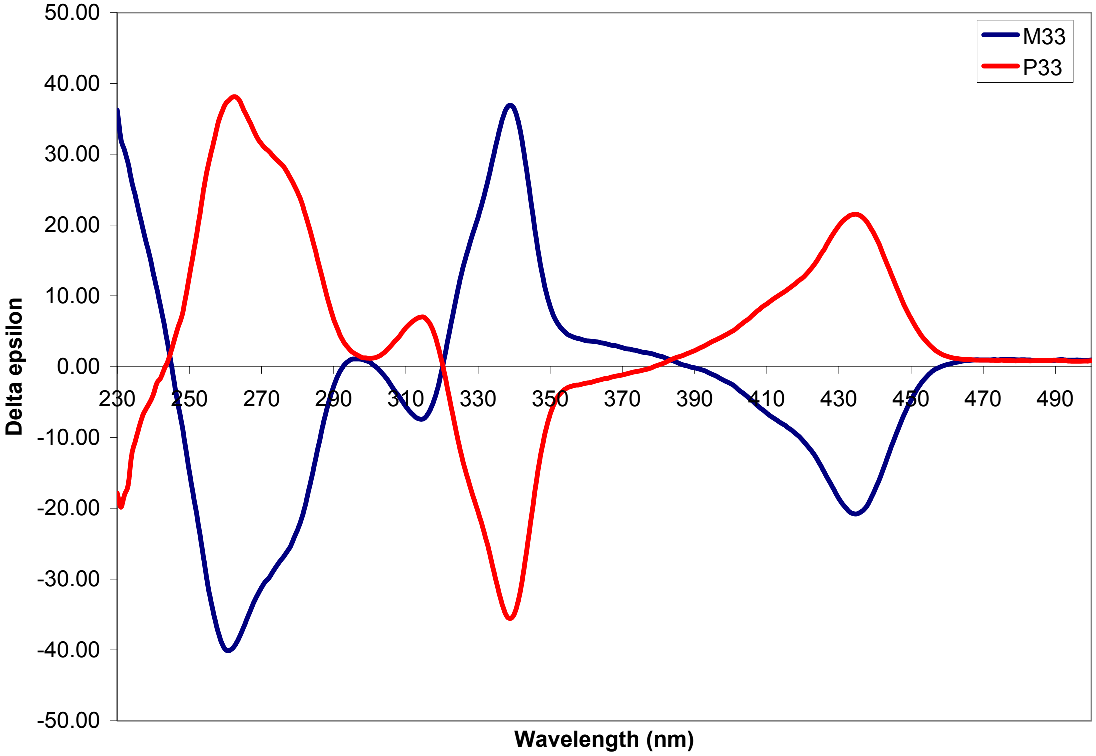


FIGURE 35. CD spectra of *M*-**33** (blue) and *P*-**33** (red) as 2.5 x 10^{-4} M solutions in $CHCl_3$.

Having separated the first in the series of the bridged triarylamine helicenes, we set out to separate the second helicene **21** in an analogous manner (Figure 36). Coupling of 1-aminonaphthalene to 2-iodoanisole gave **34** in a 66% yield, after purification by column chromatography and re-crystallization. Next, the same *tert*-butylbromodiester **16** that we used in the previous synthesis was coupled with **34** to give **35** in 30% yield. The yields of the coupling reactions were significantly lower than that observed for **33**, however, this is not surprising due to the introduction of a more sterically bulky naphthyl moiety. Subsequent hydrolysis and cyclization gave the substituted heterohelicene **36** in 66% yield. Deprotection of the methoxy group was obtained by refluxing the substrate in a mixture of hydrobromic and acetic acids to give **37** in 72% yield. Finally, (1*S*)-camphanic acid chloride was reacted with **37** to give **38** as a diastereomeric mixture of *P*- and *M*- isomers in almost quantitative yield.

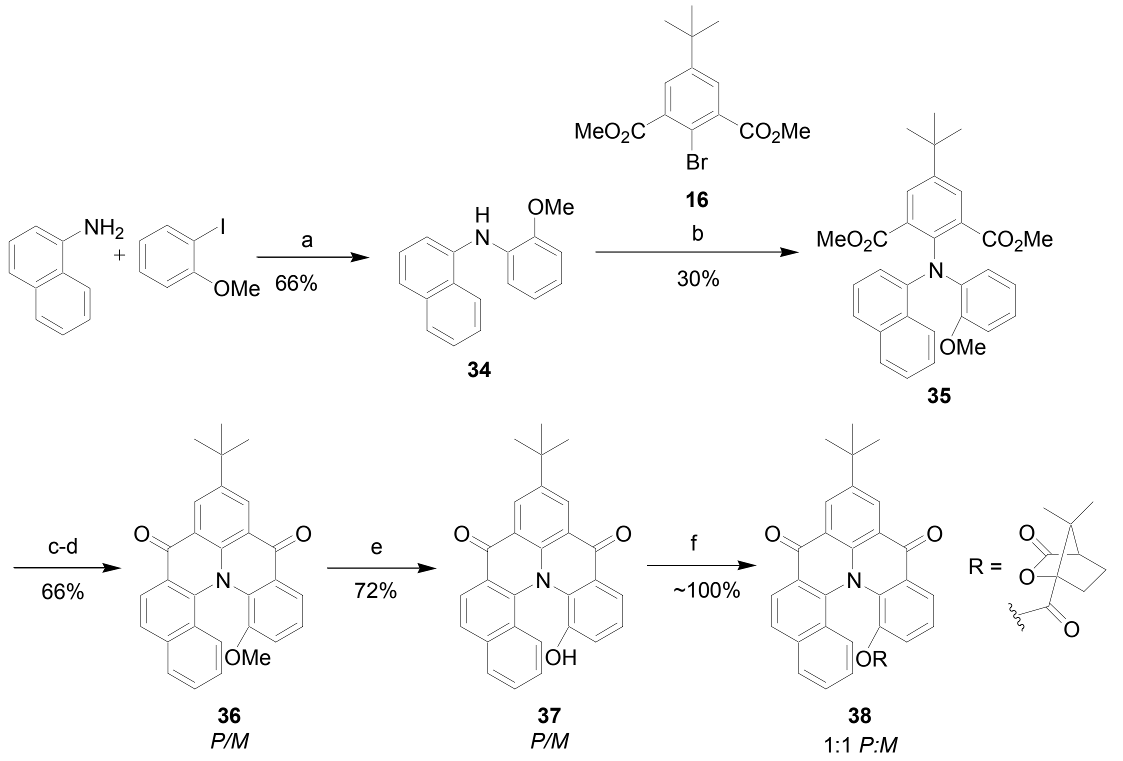


FIGURE 36. Synthesis of (1*S*)-camphanate substituted bridged triarylamine heterohelicene **38**. Reaction conditions: (a) $Pd_2(dba)_3$, DPPF, $NaOBu^t$, toluene, 110 °C; (b) Cu, CuI, K_2CO_3, $(n\text{-}Bu)_2O$, 170 °C, 3d; (c) NaOH, H_2O/EtOH (1:1), reflux then HCl; (d) $(ClCO)_2$, CH_2Cl_2, reflux 0.5 h then $SnCl_4$, reflux 2 h; (e) 1:2 AcOH:HBr, reflux, 3 d; (f) DMAP, (*S*)-Camphanic chloride, CH_2Cl_2, reflux, 12 h.

The two-dimensional TLC of **38** was similar to that shown in Figure 33. However, since the reaction went to near complete conversion, only one column (1:1 hexane/ethyl acetate) was necessary for the separation of the diastereomers. Figure 37 shows the ^{1}H-NMR of *M*-**38** (higher R_f) and *P*-**38** (lower R_f). The same trends as that observed in the spectra of the isomers of **33** hold true for **38**, namely the observed shielding effect of the camphanate methyl group in *P*-**38** by the heterohelicene.

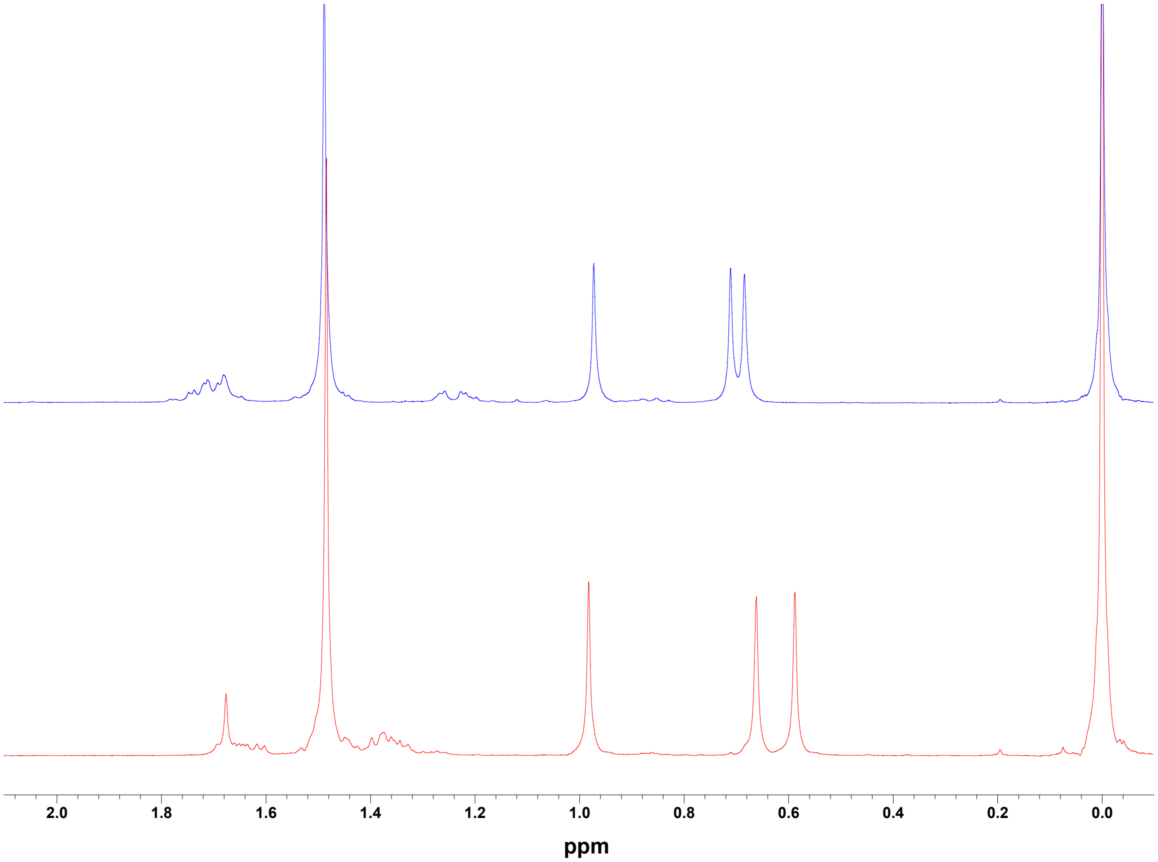


FIGURE 37. 300 MHz ^{1}H-NMR spectra of the aliphatic regions of *M*-**38** (blue) and *P*-**38** (red) in $CDCl_3$.

The CD spectra of *M*- and *P*- **38** are shown in Figure **38**. Similar to **33**, the spectra show strong absorption signals that are of opposite signs. Once again, this is definitive proof of the separation of the diastereomers of **38**.

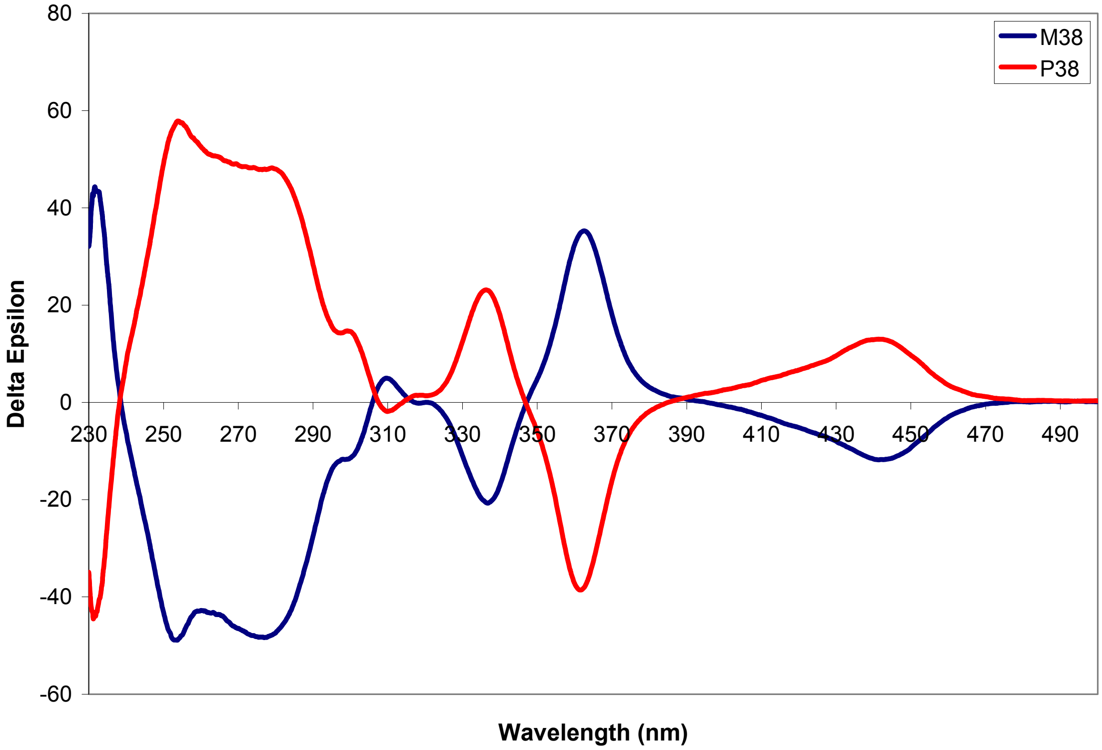


FIGURE 38. CD spectra of *M*-**38** (blue) and *P*-**38** (red) as 2.5 x 10^{-4} M solutions in $CHCl_3$.

3.8 Circularly Polarized Luminescence:

The absorption and emission spectra of *M*-**33** and *P*-**33** (Figure 39) are identical, as would be expected from these diastereomers. The absorption and emission maxima are observed at 434 and 450 nm, respectively. The small Stokes shift of 16 nm is indicative that there are no significant conformational changes that occur in the excited state.

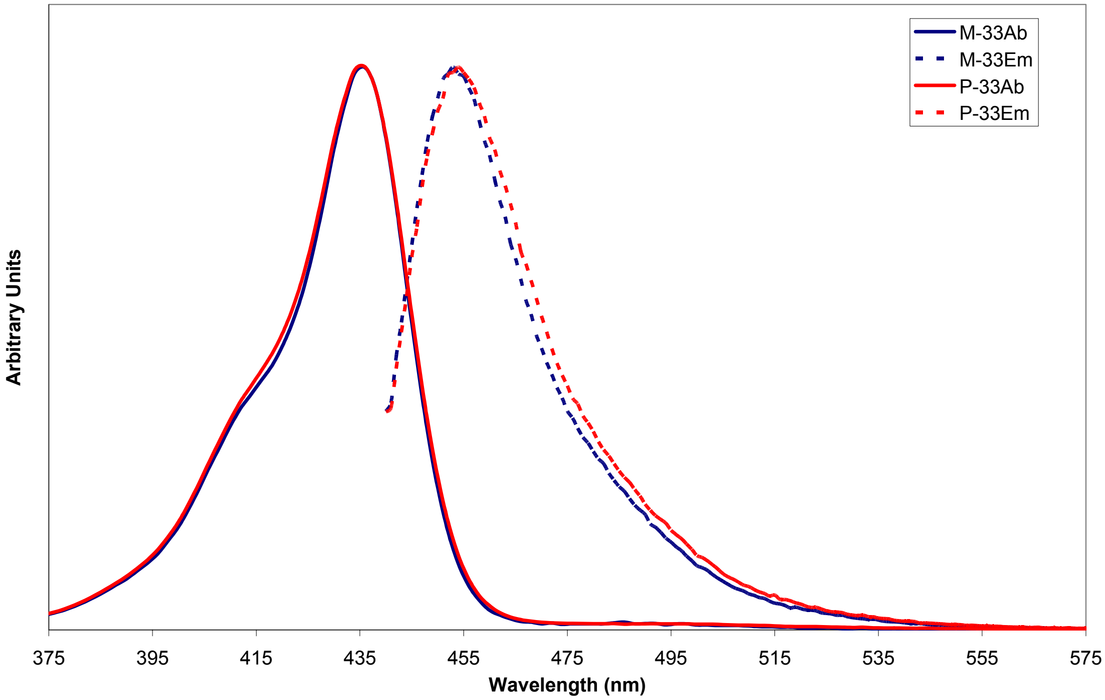


FIGURE 39. Absorption and emission spectra of *M*-**33** (blue) and *P*-**33** (red) as solutions in $CHCl_3$.

The selective absorption of circularly polarized light (CPL) is seen in the CD spectra (Figure 35), which shows that the diastereomers preferentially absorb left and right CPL in equal but opposite amounts. The degree of circular polarization in absorption, g_{abs}, is given by:

$$g_{abs} = \frac{\Delta\varepsilon}{\varepsilon} = \frac{(\varepsilon_L - \varepsilon_R)}{\varepsilon}$$

and is –0.001 and +0.001 for *M*-**33** and *P*-**33**, respectively, at the maximum wavelength of 434 nm. The analogous CPL emission spectra[54,55] were measured in $CHCl_3$ solutions at concentrations of 2×10^{-6} M at 295 K (Figure 40). The luminescence dissymmetry ratio, g_{lum}, is given by:

$$g_{lum} = \frac{\Delta I}{\frac{1}{2} I} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)}$$

where I_L and I_R refer to the intensity of left and right circularly polarized light, respectively. The g_{lum} values for *M*-**33** and *P*-**33** are –0.0011 ± 0.0002 and +0.0009 ± 0.0002, respectively, at the maximum emission wavelength of 450 nm. The fact that g_{abs} for the transition around 434 nm has the same sign as g_{lum} for the transition around 450 nm indicates that the absorption and emission originate from the same transition and corroborates the absence of significant conformational changes in the excited state indicated by the small Stokes shift.

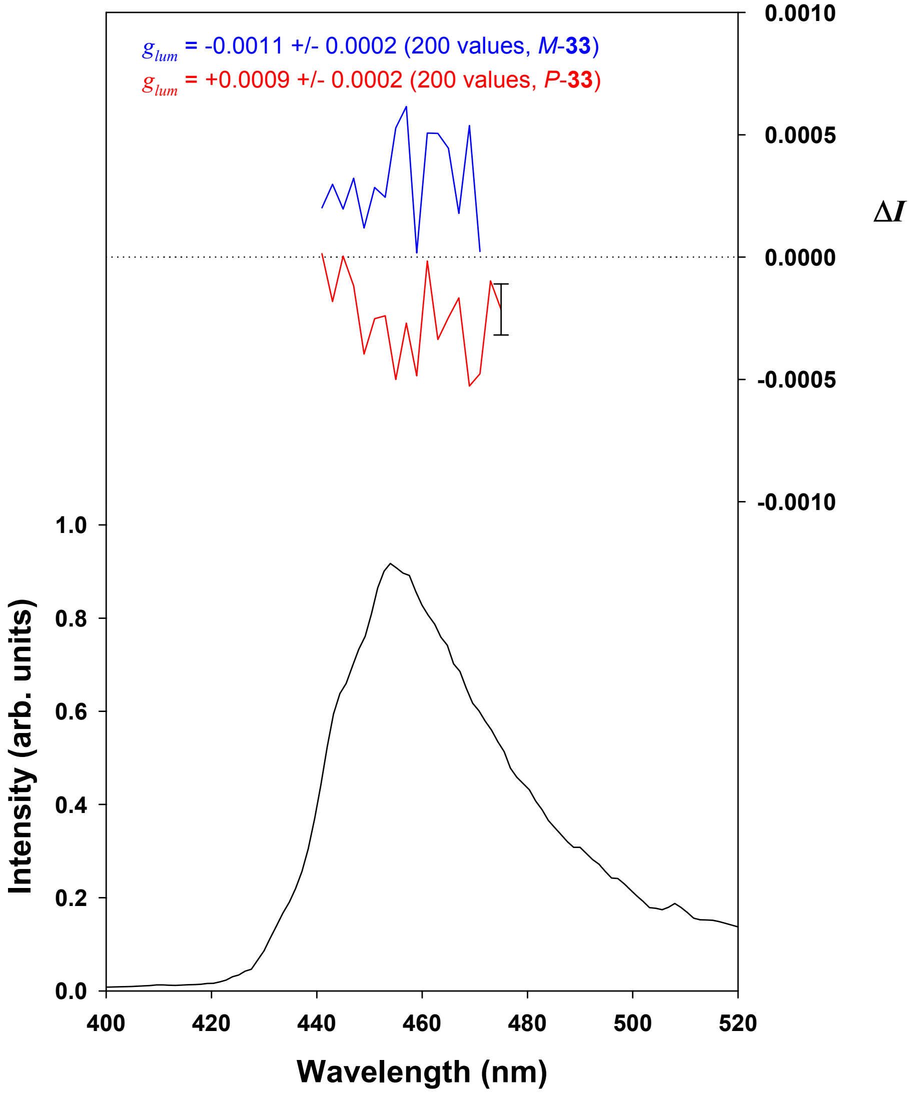


FIGURE 40. CPL emission spectra of *M*-**33** (blue) and *P*-**33** (red) as solutions in $CHCl_3$.

The absorption and emission spectra of *M*-**38** and *P*-**38** (Figure 41) are also identical. The absorption and emission maxima are observed at 443 and 478 nm, respectively. The increased Stokes shift of 35 nm could be indicative of a greater conformational change in the excited state.

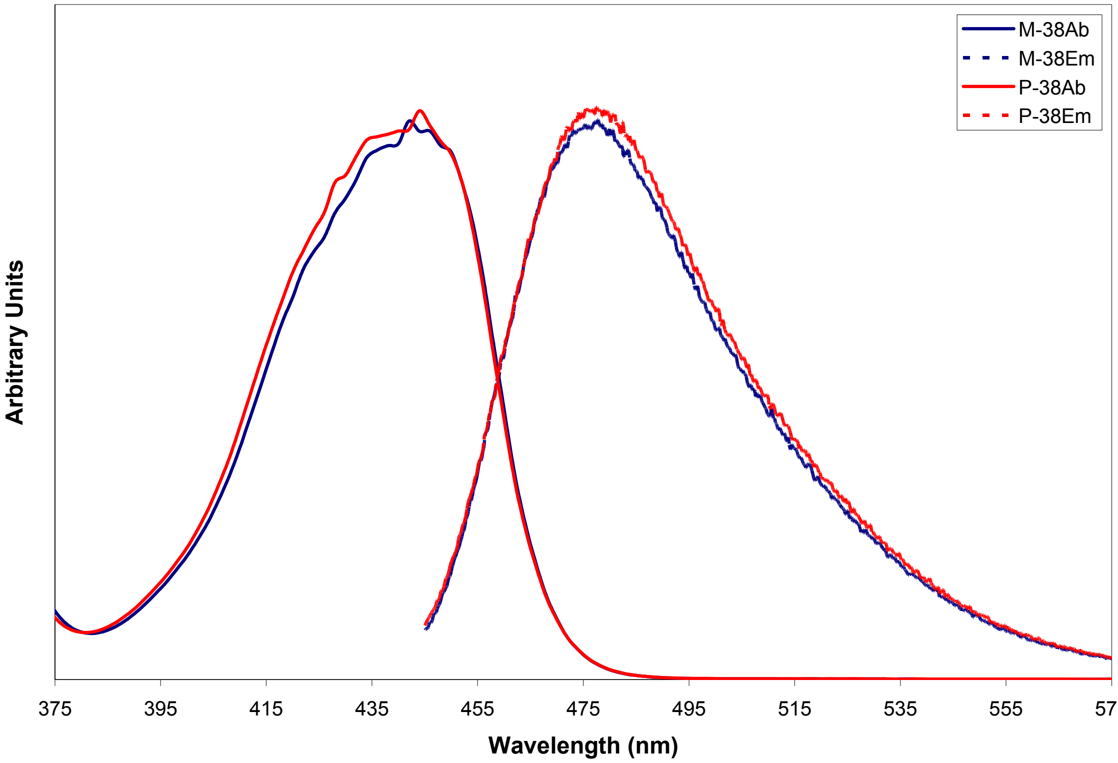


FIGURE 41. Absorption and emission spectra of *M*-**38** (blue) and *P*-**38** (red) as solutions in $CHCl_3$.

The CD spectra of *M*-**38** and *P*-**38** (Figure 38) also shows that the diastereomers preferentially absorb left and right CPL in equal but opposite amounts. The g_{abs} are about –0.0009 and +0.0009 for *M*-**38** and *P*-**38**, respectively, for the transition at 443 nm. The CPL emission spectra were measured in $CHCl_3$ solutions at concentrations of 3.3×10^{-6} M at 295 K (Figure 42). The luminescence dissymmetry ratio, g_{lum}, are -0.0007 ± 0.0002 and +0.0008 ± 0.0002 at the maximum emission wavelength of 478 nm.

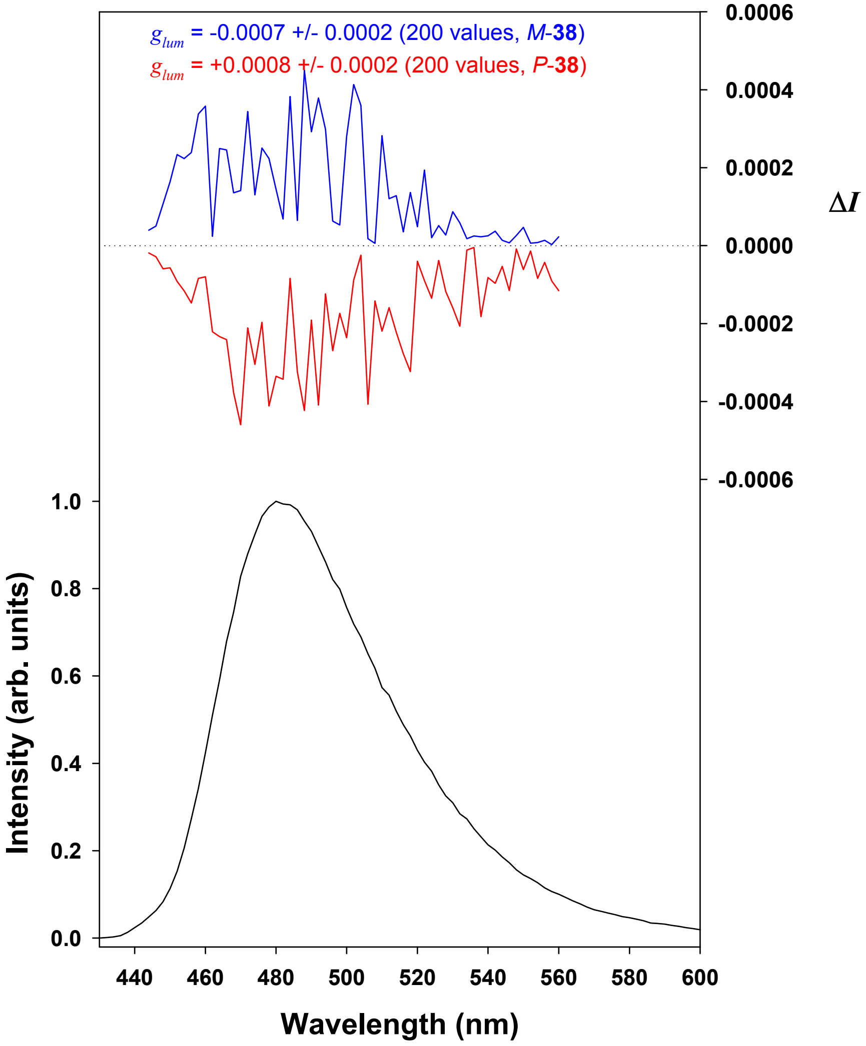
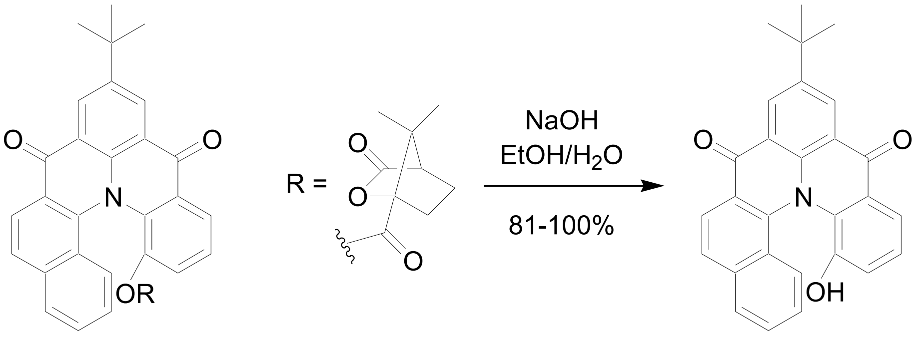


FIGURE 40. CPL emission spectra of *M*-**38** (blue) and *P*-**38** (red) as solutions in $CHCl_3$.

The lower g_{lum} was a surprising result as we had expected that the increased helical overlap of the bridged triarylamine **38** would increase the degree of CPL emission from that observed in **33**. In fact, what we observe is a decrease in the degree of CPL emission. This phenomenon has several possible explanations. The first possibility may be that although the additional aromatic ring may increase the helicity of the molecule, it may also affect the electronic structure of the chromophore in a negative manner, possibly causing a significant change in conformation of the excited state.

Another explanation was proposed by Katz.[12] Since the sample is measured as a dilute solution, the molecules may have time to rotate and/or tumble after excitation and before emission, possibly causing a decrease in the CPL emission observed. This would agree with the results observed by Katz for aggregating helicenes, which as dilute solutions show low CPL emission (g_{lum} = 0.001) but exhibit a 10 fold increase in CPL (g_{lum} = 0.01) as aggregates with limited rotational freedom. Thus, it stands to reason, that the CPL emission of our molecules may be more accurately measured in a solid, gel, aggregated, or even viscous state. Unfortunately, this hypothesis is contrary to the known theory of CPL measurement which predicts that an increased ordering will increase the linear polarization of the emission, making it nearly impossible to accurately measure the CPL. This is indeed the case in the experiment by Katz who reports an increase in linear polarization from P = 0.02 to P = 0.39 (0.5 is the maximum polarization). Thus the observed g_{lum} = 0.01 for the aggregates is questionable at best.

Since the CPL emission arises from an electron undergoing an electronic transition along a helical path, it may be possible to increase the CPL emission by modifying the size of the helical chromophore. This can be achieved in three ways: i) increase the pitch of the helix, ii) increase the diameter of the helix, and/or iii) increase the length of the helix. With this in mind, we set out to link our separated helicenes together to form a larger, dimeric system. The first step was to remove the camphanate groups without racemizing the atropisomers. This was achieved through a simple base-hydrolysis of *P*- and *M*-**38** carried out at room temperature in order to avoid racemization (Figure 41).



38
P- or *M*-

37
P- or *M*-

FIGURE 41. Hydrolysis of *P*- and *M*-**38** to give *P*- and *M*-**37**.

To ensure that the helicene alcohols (**37**) remained chiral, the CD spectra were obtained (Figure 42). The spectra illustrate that the helicene alcohols do indeed remain chiral as indicated by their opposite signals. Also, the signals appear to be much weaker, possibly due to the decreased helical pitch of the helicene as a result of the removal of the bulky camphanate group.

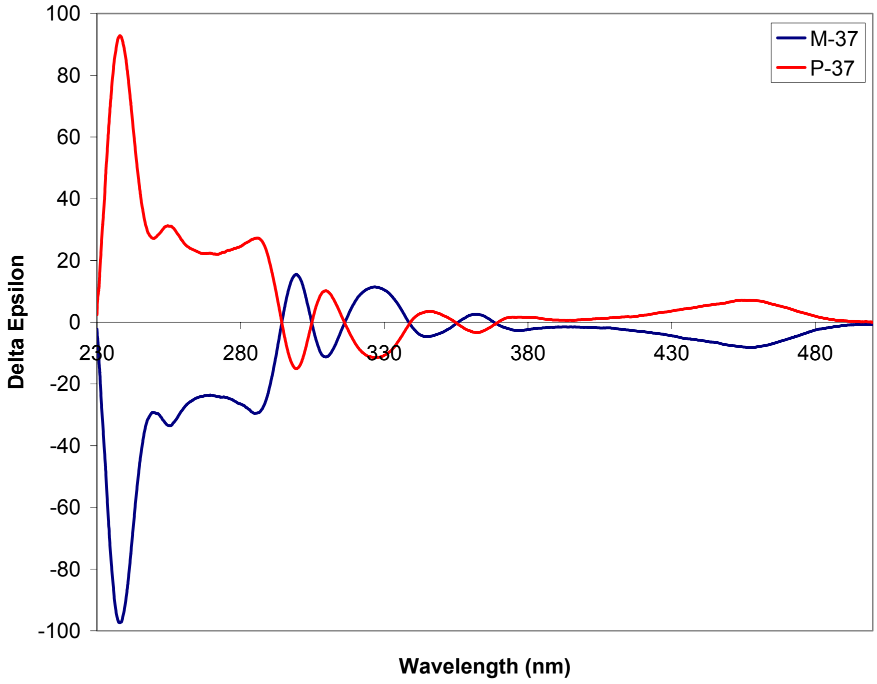
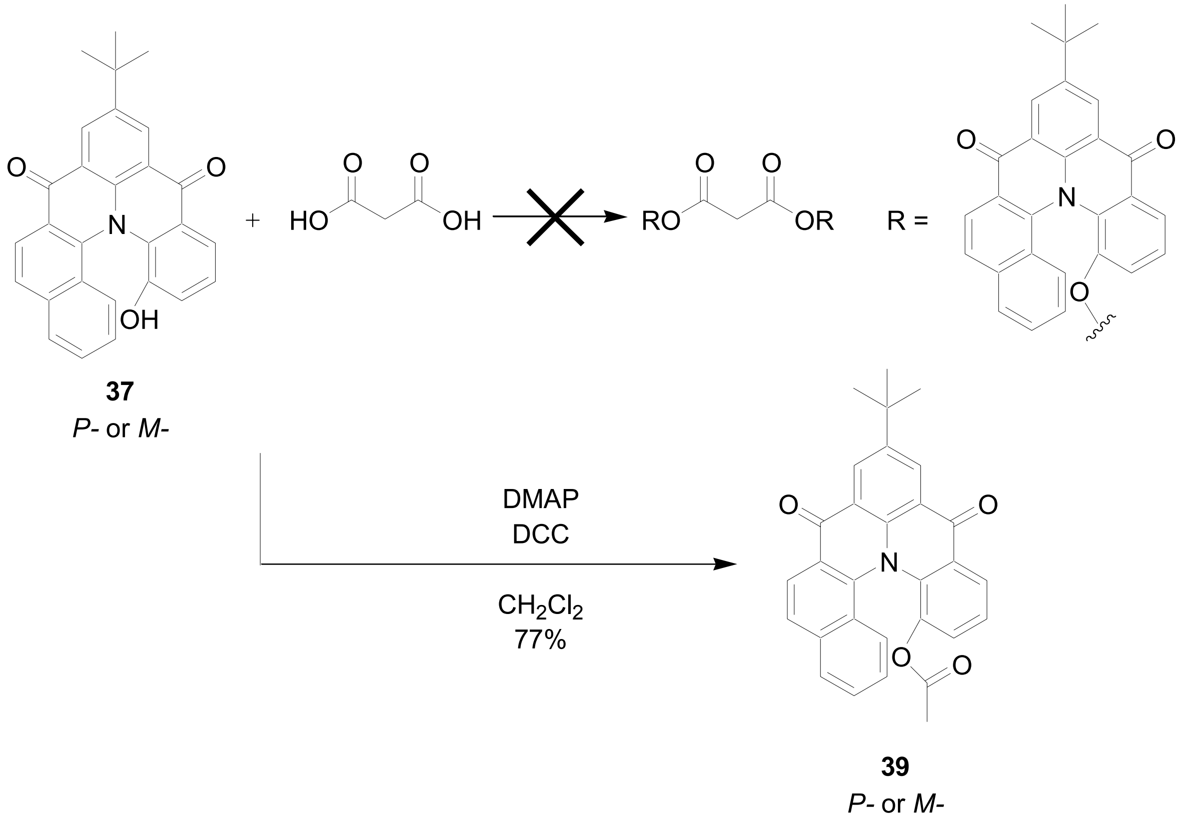


FIGURE 42. CD spectra of *M*-**37** (blue) and *P*-**37** (red) as solutions in CHCl$_3$.

The chiral, helicene alcohol *M*-**37** was coupled to malonic acid (Figure 43) using N,N-dimethylaminopyridine (DMAP) and N,N'-dicyclohexylcarbodiimide (DCC) in dichloromethane in an attempt to obtain a dimer. Surprisingly, the reaction did not yield a dimer but rather the methyl ester derivative **39**. We hypothesize that this product is a result of an intramolecular cyclization of malonic acid with DCC which decomposes to the methyl ester **39**, CO_2, and dicyclohexylurea (DHU) upon attack of one of the carbonyls by the helicene alcohol (Figure 44).



37
P- or *M*-

39
P- or *M*-

FIGURE 43. The reaction of **37** with malonic acid in the presence of DMAP and DCC.

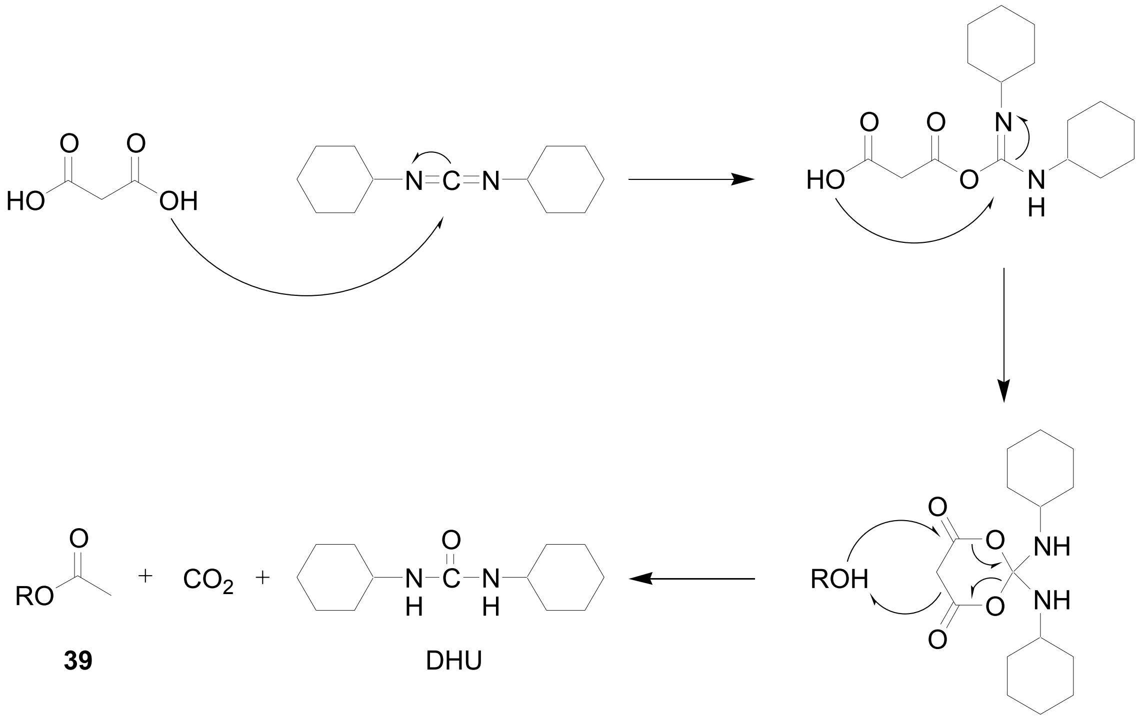


FIGURE 44. The proposed mechanism for the formation of **39**.

In order to obtain the desired dimeric system, it was necessary to employ the acid chloride derivative of malonic acid. However, this compound was temporarily unavailable and so we thus employed succinyl chloride instead. The coupling of *M*-**37** to succinyl chloride proceeded in 87% yield.

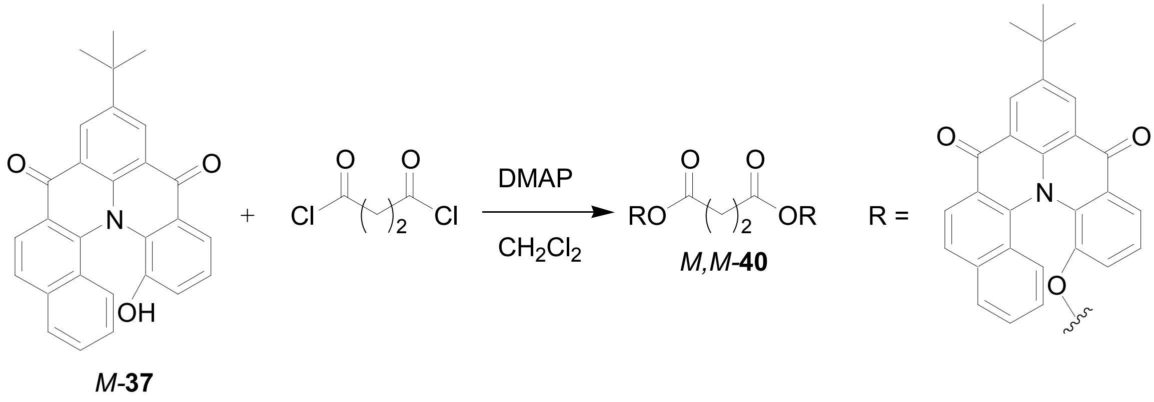


FIGURE 45. Synthesis of *M,M*-**40**.

The CD and absorption spectra of *M,M*-**40** (Figure 46) show similar signals to those of *M*-**38**. This further supports our assertion that the observed signals mainly arise from electronic transitions of the helicene chromophore rather than the camphanate substituents used to separate them. *M,M*-**40** shows a g_{abs} of -0.0006 which is similar to that observed for *M*-**38**. This is surprising as we had anticipated that a dimeric system would contribute to a larger helical structure and thus result in a higher degree of polarization in the CD spectrum.

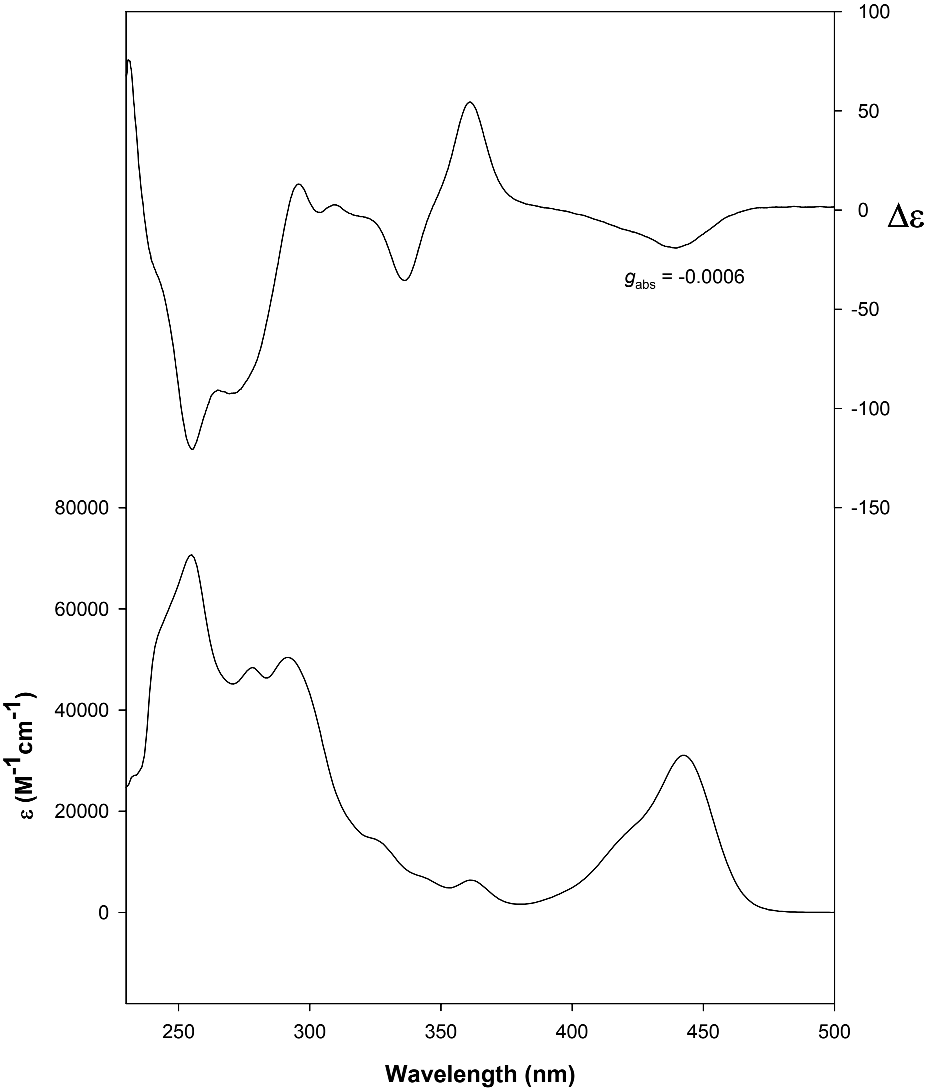


FIGURE 46. Absorption and CD Spectra of *M,M*-**40** in $CHCl_3$.

3.9 Conclusion:

To summarize our results, we have developed an efficient synthesis of a new class of heterohelicenes based on bridged triarylamines. Furthermore, we have studied the solid-state structure, photochemical, and electrochemical properties of these molecules. Unlike any other carbo- or heterohelicene,[3,56-64] these systems show the ability to be oxidized to stable radical cations. This property makes these chromophores attractive as emissive hole-conduction materials for applications such as organic light-emitting diodes. Future effort should focus on separation of these atropisomers in order to determine the barrier of racemisation.[65,66]

We have also synthesized derivatives with camphanate substituents that allow for separation by standard column chromatography. These separated diastereomers show preferential absorption and emission of circularly polarized light. Such properties may possibly be utilized for back-lighting in liquid-crystalline displays (LCD) (Figure 47).[13,15,67] For instance, a traditional LCD uses a polarizer to convert unpolarized light to polarized light that can then be passed though a liquid-crystalline (LC) material. The LC material can either allow the polarized light to pass through unchanged or rotate it by 90°. It then passes through a second polarizer that will either allow it to pass through unchanged or filter it out completely, depending on its orientation as determined by the LC layer. Since these polarizers are large, expensive to manufacture, and inefficient (they filter out greater than 50% of the light), a significant improvement could be made by introducing a back-lighting source that was already polarized. Such a back-lighting device could be made using the chiral bridged triarylamine helicenes as the emissive/hole-transport layer in a standard OLED. The CPL emission could easily be transformed into linearly polarized light using a quarter-wave plate with little loss of intensity.[13] Alternatively, an LC phase could be developed that could manipulate CPL directly rather than linearly polarized light. Such hybrid devices would merge the dominant LCD technology with the emerging OLED technology.

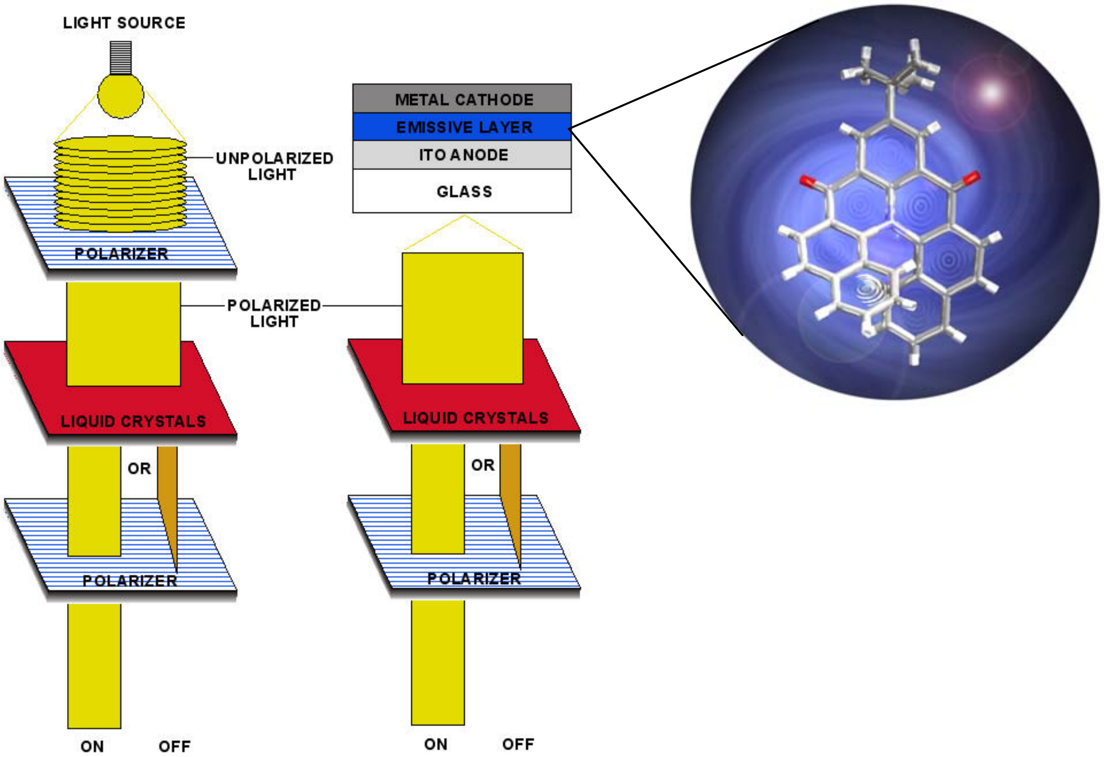


FIGURE 47. Typical LCD (left) and hybrid OLED/LCD with polarized back-lighting (right) from a bridged triarylamine heterohelicene (right inset).

3.10 References:

(1) Newman, M. S.; Lednicer, D. "The Synthesis and Resolution of Hexahelicene" *J. Am. Chem. Soc.* **1956**, *78*, 4765-4770.

(2) Newman, M. S.; Lutz, W. B.; Lednicer, D. "A New Reagent for Resolution by Complex Formation; The Resolution of Phenanthro-[3,4-c]Phenanthrene" *J. Am. Chem. Soc.* **1955**, *77*, 3420-3421.

(3) Laarhoven, W. H.; Prinsen, W. J. C. "Carbohelicenes and Heterohelicenes" *Top. Curr. Chem.* **1984**, *125*, 63-130.

(4) Meurer, K. P.; Vogtle, F. "Helical Molecules in Organic-Chemistry" *Top. Curr. Chem.* **1985**, *127*, 1-76.

(5) Rowan, A. E.; Nolte, R. J. M. "Helical molecular programming" *Angew. Chem. Int. Ed.* **1998**, *37*, 63-68.

(6) Katz, T. J. "Syntheses of functionalized and aggregating helical conjugated molecules" *Angew. Chem. Int. Ed.* **2000**, *39*, 1921-1923.

(7) Murguly, E.; McDonald, R.; Branda, N. R. "Chiral discrimination in hydrogen-bonded 7 helicenes" *Org. Lett.* **2000**, *2*, 3169-3172.

(8) Owens, L.; Thilgen, C.; Diederich, F.; Knobler, C. B. "A New Helicopodand - Molecular Recognition of Dicarboxylic- Acids with High Diastereoselectivity" *Helv. Chim. Acta* **1993**, *76*, 2757-2774.

(9) Weix, D. J.; Dreher, S. D.; Katz, T. J. "5 HELOL phosphite: A helically grooved sensor of remote chirality" *J. Am. Chem. Soc.* **2000**, *122*, 10027-10032.

(10) Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. "Strong enhancement of nonlinear optical properties through supramolecular chirality" *Science* **1998**, *282*, 913-915.

(11) Nuckolls, C.; Katz, T. J. "Synthesis, structure, and properties of a helical columnar liquid crystal" *J. Am. Chem. Soc.* **1998**, *120*, 9541-9544.

(12) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. "Synthesis and properties of an aggregating heterocyclic helicene" *J. Am. Chem. Soc.* **2001**, *123*, 11899-11907.

(13) Grell, M.; Bradley, D. D. C. "Polarized luminescence from oriented molecular materials" *Adv. Mater.* **1999**, *11*, 895-905.

(14) Montali, A.; Bastiaansen, G.; Smith, P.; Weder, C. "Polarizing energy transfer in photoluminescent materials for display applications" *Nature* **1998**, *392*, 261-264.

(15) Dyreklev, P.; Berggren, M.; Inganas, O.; Andersson, M. R.; Wennerstrom, O.; Hjertberg, T. "Polarized Electroluminescence from an Oriented Substituted Polythiophene in a Light-Emitting Diode" *Adv. Mater.* **1995**, *7*, 43-45.

(16) Bolognesi, A.; Botta, C.; Facchinetti, D.; Jandke, M.; Kreger, K.; Strohriegl, P.; Relini, A.; Rolandi, R.; Blumstengel, S. "Polarized electroluminescence in double-layer light-emitting diodes with perpendicularly oriented polymers" *Adv. Mater.* **2001**, *13*, 1072-1075.

(17) Eskildsen, J.; Krebs, F. C.; Faldt, A.; Sommer-Larsen, P.; Bechgaard, K. "Preparation and structural properties of 7,8-dioxa 6 helicenes and 7a,14c-dihydro-7,8-dioxa 6 helicenes" *J. Org. Chem.* **2001**, *66*, 200-205.

(18) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. "Annelated heptathiophene: A fragment of a carbon-sulfur helix" *Angew. Chem. Int. Ed.* **2000**, *39*, 4481-4483.

(19) Tanaka, K.; Kitahara, Y. "Self-assembly of (P)-heterohelicenediol into a four-leaf clover motif" *Chem. Commun.* **1998**, 1141-1142.

(20) Staab, H. A.; Diehm, M.; Krieger, C. "Synthesis, Structure and Basicity of 1,16-Diaza 6 Helicene" *Tetrahedron Lett.* **1994**, *35*, 8357-8360.

(21) Caronna, T.; Gabbiadini, S.; Mele, A.; Recupero, F. "Approaches to the azahelicene system: Synthesis and spectroscopic characterization of some diazapentahelicenes" *Helv. Chim. Acta* **2002**, *85*, 1-8.

(22) Norsten, T. B.; Peters, A.; McDonald, R.; Wang, M. T.; Branda, N. R. "Reversible 7 -thiahelicene formation using a 1,2- dithienylcyclopentene photochrome" *J. Am. Chem. Soc.* **2001**, *123*, 7447-7448.

(23) Caronna, T.; Sinisi, R.; Catellani, M.; Malpezzi, L.; Meille, S. V.; Mele, A. "Photochemical synthesis and structural properties of high membered thiohelicenes" *Chem. Commun.* **2000**, 1139-1140.

(24) Harrowven, D. C.; Nunn, M. I. T.; Fenwick, D. R. "5 Helicenes by iterative radical cyclisations to arenes" *Tetrahedron Lett.* **2002**, *43*, 3189-3191.

(25) Dopper, J. H.; Oudman, D.; Wynberg, H. "Use of thieno[2,3-b]thiophene in the synthesis of heterohelicenes by double photocyclizations" *J. Am. Chem. Soc.* **1973**, *95*, 3692-3698.

(26) Katz, T. J.; Liu, L. B.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S. H.; Nuckolls, C.; Rickman, B. H. "An efficient synthesis of functionalized helicenes" *J. Am. Chem. Soc.* **1997**, *119*, 10054-10063.

(27) Treboux, G.; Lapstun, P.; Wu, Z. H.; Silverbrook, K. "Electronic conductance of helicenes" *Chem. Phys. Lett.* **1999**, *301*, 493-497.

(28) Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. "New triarylamine-containing polymers as hole transport materials in organic light-emitting diodes: Effect of polymer structure and cross-linking on device characteristics" *Chem. Mater.* **1998**, *10*, 1668-1676.

(29) Hellwinkel, D.; Melan, M. "Heteropolycyclic compounds of the triangulene type. I. 8,12-Dihydro-4H-benzo[1,9]quinolizino[3,4,5,6,7-difg]acridine-4,8,12-trione and 5,9-dihydroquino[3,2,1-de]acridine-5,9-dione" *Chem. Ber.* **1971**, *104*, 1001-1016.

(30) Hellwinkel, D.; Schmidt, W. "Modified tetrahelicene systems. III. Doubly ortho-bridged triphenylamine derivatives" *Chem. Ber.* **1980**, *113*, 358-384.

(31) Field, J. E.; Venkataraman, D. "Heterotriangulenes - Structure and properties" *Chem. Mater.* **2002**, *14*, 962-964.

(32) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. "Anodic Oxidation Pathways of Aromatic Amines. Electrochemical and Electron Paramagnetic Resonance Studies" *J. Am. Chem. Soc.* **1966**, *88*, 3498-3503.

(33) Faber, R.; Mielke, G. F.; Rapta, P.; Stasko, A.; Nuyken, O. "Anodic oxidation of novel hole-transporting materials derived from tetraarylbenzidines. Electrochemical and spectroscopic characterization" *Collect. Czech. Chem. Commun.* **2000**, *65*, 1403-1418.

(34) Benin, V. A.; Martin, J. C.; Willcott, M. R. "Solution and solid state studies of some new silicon and germanium compounds stabilized by tridentate ligands" *Tetrahedron* **1997**, *53*, 10133-10154.

(35) Tashiro, M.; Yamato, T. "Studies on selective preparation of aromatic compounds. Part 16. A convenient preparation of 1,2-di- and 1,2,3-trisubstituted benzenes using the tert-butyl function as a positional protective group" *J. Chem. Soc. Perkin Trans. 1* **1972**, 176-179.

(36) Yoshifuji, M.; Nakazawa, M.; Sato, T.; Toyota, K. "Formation and rearrangement of dithioxo- and diselenoxophosphoranes carrying bulky 4-t-butyl-2,6-bis(methoxyalkyl)phenyl groups" *Tetrahedron* **2000**, *56*, 43-55.

(37) Hartwig, J. F. "Carbon-heteroatom bond-forming reductive eliminations of amines, ethers, and sulfides" *Acc. Chem. Res.* **1998**, *31*, 852-860.

(38) Hartwig, J. F. "Transition metal catalyzed synthesis of arylamines and aryl ethers from aryl halides and triflates: Scope and mechanism" *Angew. Chem. Int. Ed.* **1998**, *37*, 2047-2067.

(39) Muci, A. R.; Buchwald, S. L. *"*Practical palladium catalysts for C-N and C-O bond formation*",Cross-Coupling Reactions, Vol. 219*, **2002**; pp 131-209.

(40) Yang, B. H.; Buchwald, S. L. "Palladium-catalyzed amination of aryl halides and sulfonates" *J. Organomet. Chem.* **1999**, *576*, 125-146.

(41) Field, J. E.; Venkataraman, D. "Helix versus zig-zag: control of supramolecular topology via carboxylic acid conformations in ortho-substituted phenyl amines" *Chem. Commun.* **2002**, 306-307.

(42) Lai, Y. H. "Synthesis and Diatropicity of a Phenanthrene-Annelated Trans-Dimethyldihydropyrene - a Novel Molecule to Indicate the High Pi-Bond Order of the 9,10 Bond of Phenanthrene" *J. Am. Chem. Soc.* **1985**, *107*, 6678-6683.

(43) Dapperheld, S.; Steckhan, E.; Brinkhaus, K. H. G.; Esch, T. "Organic Electron-Transfer Systems .2. Substituted Triarylamine Cation-Radical Redox Systems - Synthesis, Electrochemical and Spectroscopic Properties, Hammet Behavior, and Suitability as Redox Catalysts" *Chem. Ber.* **1991**, *124*, 2557-2567.

(44) Selby, T. D.; Kim, K. Y.; Blackstock, S. C. "Patterned redox arrays of polyarylamines I. Synthesis and electrochemistry of a p-phenylenediamine and arylamino-appended p-phenylenediamine arrays" *Chem. Mater.* **2002**, *14*, 1685-1690.

(45) Thongpanchang, T.; Paruch, K.; Katz, T. J.; Rheingold, A. L.; Lam, K. C.; Liable-Sands, L. "Why (1S)-camphanates are excellent resolving agents for helicen-1-

ols and why they can be used to analyze absolute configurations" *J. Org. Chem.* **2000**, *65*, 1850-1856.

(46) Lightner, D. A.; Gurst, J. E. "Organic Conformational Analysis and Stereochemistry from Circular Dichroism Spectroscopy*" Methods in Stereochemical Analysis Vol.* Marchand, A. P.; John Wiley & Sons: New York, **2000**, 37-62.

(47) Weigang, O. E.; Turner, J. A.; Trouard, P. A. "Emission Polarization and Circular Dichroism of Hexahelicene" *J. Chem. Phys.* **1966**, *45*, 1126-1134.

(48) Newman, M. S.; Darlak, R. S.; Tsai, L. "Optical Properties of Hexahelicene" *J. Am. Chem. Soc.* **1967**, *89*, 6191-6193.

(49) Wynberg, H.; Groen, M. B. "Synthesis, Resolution, and Optical Rotary Dispersion of a Hexa- and a Heptaheterohelicene" *J. Am. Chem. Soc.* **1968**, *90*, 5339-5341.

(50) Groen, M. B.; Wynberg, H. "Optical Properties of Some Heterohelicenes. The Absolute Configuration" *J. Am. Chem. Soc.* **1971**, *93*, 2968-2974.

(51) Brown, A.; Kemp, C. M.; Mason, S. F. "Electronic Absorption, Polarised Excitation, and Circular Dichroism Spectra of [5]-Helicene (Dibenzo[*c,g*]phenanthrene)" *J. Chem. Soc.* **1971**, 751-755.

(52) Brickell, W. S.; Brown, A.; Kemp, C. M.; Mason, S. F. "pi-Electron Absorption and Circular Dichroism Spectra of [6]- and [7]-Helicene" *J. Chem. Soc.* **1971**, 756-760.

(53) Yamada, K.-I.; Tanaka, H.; Nakagawa, H.; Ogashiwa, S.; Kawazura, H. "NMR and CD Spectral Features of Thiaheterohelicenes. Effect of Intramolecular Overlap of Aromatic Rings" *Bull. Chem. Soc. Jpn.* **1982**, *55*, 500-503.

(54) Riehl, J. P.; Richardson, F. S. "Circularly Polarized Luminescence Spectroscopy" *Chem. Rev.* **1986**, *86*, 1-16.

(55) Riehl, J. P.; Richardson, F. S. *"*Circularly-Polarized Luminescence*",Metallobiochemistry, Part C, Vol. 226*, **1993**; pp 539-553.

(56) Laarhoven, W. H.; Brus, G. J. M. "Polarographic Data and Deviations from Coplanarity of Helicene Molecules" *J. Chem. Soc.* **1971**, 1433-1434.

(57) Weissman, S. I.; Chang, R. "Optical and magnetic properties of anions of hexahelicene" *J. Am. Chem. Soc.* **1972**, *94*, 8683-8685.

(58) Fey, H. J.; Kurreck, H.; Lubitz, W. "ENDOR studies of [6]helicene anion radical" *Tetrahedron* **1979**, *35*, 905-907.

(59) Kim, S. S.; Weissman, S. I. "Intersystem crossing in hexahelicene" *J. Am. Chem. Soc.* **1979**, *101*, 5863-5864.

(60) Diesveld, J. W.; Borkent, J. H.; Laarhoven, W. H. "The oxidation of hexahelicenes. Synthesis of hexahelicene-5,6-quinone" *Recl.Trav. Chim. Pays-Bas* **1980**, *99*, 391-394.

(61) Tanaka, H.; Ogashiwa, S.; Kawazura, H. "Electron spin resonance of thiaheterohelicene radical anions" *Chem. Lett.* **1981**, *5*, 585-588.

(62) Liberko, C. A.; Miller, L. L.; Katz, T. J.; Liu, L. B. "The Electronic-Structure of Helicene Bisquinone Anion Radicals" *J. Am. Chem. Soc.* **1993**, *115*, 2478-2482.

(63) Yang, B. W.; Liu, L. B.; Katz, T. J.; Liberko, C. A.; Miller, L. L. "Electron Delocalization in Helical Quinone Anion Radicals" *J. Am. Chem. Soc.* **1991**, *113*, 8993-8994.

(64) Laali, K. K.; Houser, J. J. "Electrophilic and Oxidative Chemistry of 4-Methyl 6 Helicene, 6 Helicene and Coronene - Persistent Ion Generation in Superacid Media, Gas-Phase Mass-Spectrometric Studies and Am1 Calculations" *J. Chem. Soc. Perkin Trans. 2* **1994**, 1303-1308.

(65) Frim, R.; Zilber, G.; Rabinovitz, M. "Helicene Dianions - the Effect of Charge on the Barrier to Racemization" *Chem. Commun.* **1991**, 1202-1203.

(66) Janke, R. H.; Haufe, G.; Wurthwein, E. U.; Borkent, J. H. "Racemization barriers of helicenes: A computational study" *J. Am. Chem. Soc.* **1996**, *118*, 6031-6035.

(67) Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H.; Meijer, E. W. "Circularly polarized electroluminescence from a polymer light-emitting diode" *J. Am. Chem. Soc.* **1997**, *119*, 9909-9910.

CHAPTER 4

DIRECTING THE ASSEMBLY OF SUPRAMOLECULAR ARCHITECTURES OF ARYLAMINES

4.1 Introduction:

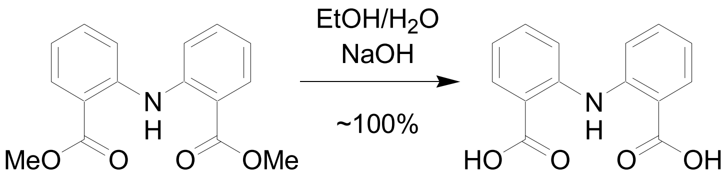
There has been an explosion of interest in the field of supramolecular chemistry over the past decade. Whether it is termed “self-assembly”,[1] “crystal-engineering”,[2] or “nano-technology”,[3] the goal is the same: to control the solid state architectures of molecular materials. It has been long known that the properties of molecular materials are not only dependent on the structure of the constituent molecule, but also on the bulk structure of the material (i.e. how the constituents interact with one another). The advances of organic chemistry have given chemists almost absolute control of molecular structure, the challenge now is to be able to control the supramolecular structure. This challenge is made remarkably difficult due to the complex nature of weak solid state interactions. However, many advances have recently been made in the field of supramolecular chemistry. One of the most important has been the identification of supramolecular synthons as building blocks based on their symmetry and intermolecular interaction components.[2] Using these tools, supramolecular chemists have explored the assembly of functional materials for catalysis,[4] biomimetics,[1,3-5] electronic and electro-optic materials,[4,6,7] molecular encapsulation,[8] and countless other applications.

Topologies such as extended helices,[9-16] Platonic and Archimedean polyhedra,[17-24] porous networks,[22,25-30] and other highly ordered architectures are highly sought after. By combining the control of molecular structure through modern organic chemistry and the control of solid state structure using supramolecular chemistry, the design of functional materials will become a more rational one, approaching the material from the bulk structure down to the molecular level.[4] Our goal here is to examine the directed assembly of arylamines, a class of molecules that has found wide application as functional electronic materials.[31, 32]

4.2 Zig-Zag Versus Helical Topologies:

Of all of nature's structures, there is arguably none more beautiful or widely scrutinized than the helix. Chemists have been attempting to mimic the helical motif in supramolecular assemblies in order to achieve functional materials.[1,4,9-16,33] With the development of crystal engineering,[2] chemists have identified a large number of intermolecular interactions to assemble targeted supramolecular motifs. Hydrogen-bonding is often applied in this regard due to the strength, directionality, and specificity of the interaction,[34] as well as its ubiquitous presence in naturally occurring assemblies. The major challenge that chemists face in creating predictable supramolecular assemblies from small molecules is to decipher nature's hierarchy of molecular interactions. It was our goal to manipulate an intramolecular interaction in order to control the conformation of an intermolecular interaction and thus provide a route to a predictable solid-state motif.[35]

During the development of the higher dimensional electronic materials described previously (see Chapter 2), we had occasion to isolate **41** from the base hydrolysis of **1** (Figure 48). This molecule formed large, well defined crystals after recrystallization from ethanol. Single crystal X-ray diffraction showed that this molecule packs in a zig-zag motif (Figure 49) which we initially mistook as the similar helical topology. Upon realizing our error, we posed the question; "How can we direct the packing of these types of systems towards the helical architecture?". To answer this question, we decided to examine the effect of the conformations of the carboxylic acid moieties on the supramolecular structure by modifying the intramolecular hydrogen-bonding to the bridging group.



1 **41**

Figure 48. The base hydrolysis of **1** to give **41**.

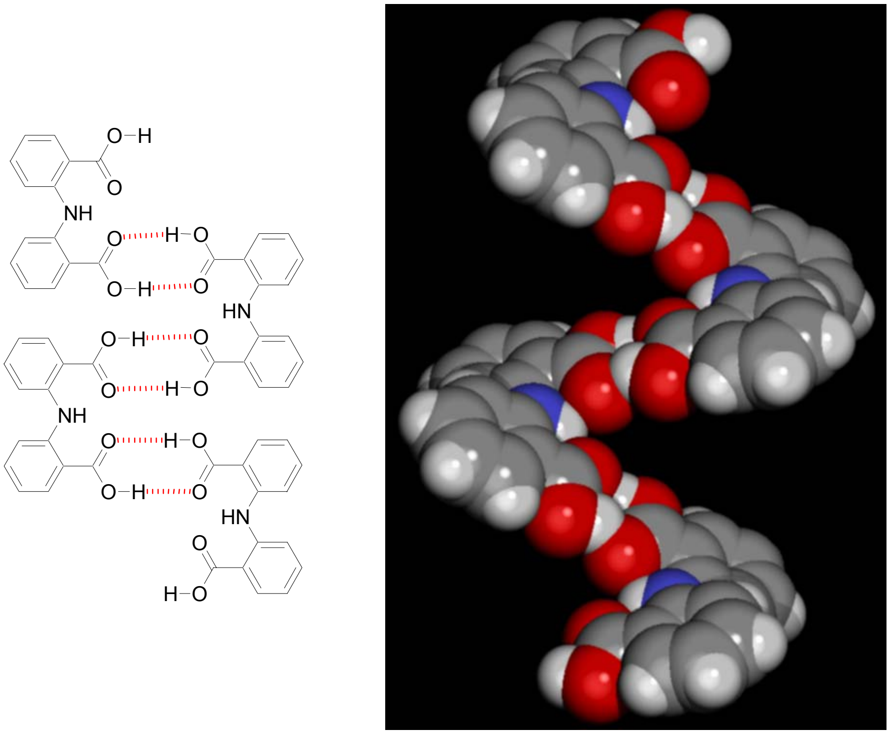


Figure 49. The zig-zag hydrogen-bonding motif of **41** (left) from the single crystal X-ray diffraction (right).

There is some precedence to using the directionality of hydrogen bonds to control supermolecular structure. For example, Wuest and co-workers have utilized symmetric and asymmetric dipyridones to control dimerization versus extended structure formation.[36-38] Our goal was to take this idea one step further by controlling the conformation of a carboxylic acid hydrogen-bond synthon using an intramolecular interaction.[39, 40] Figure 50 shows three possible packing motifs of a bis(benzoic acid) system. Motif I is composed of two atropisomers and results in a zig-zag structure.

Motifs II and III contain only a single atropisomer assembled as a trigonal coil and a circular helix respectively. The packing motifs available to this system are further limited by the three possible conformations of the carboxylic acids. The two symmetric conformations, with the carbonyls pointing in opposing directions, can only pack in motifs I or II due to the allowed intermolecular hydrogen bonding. In contrast, the asymmetric conformation, with the carbonyls both pointing in the same direction, can potentially pack in any of the three motifs. We set out to synthesize a series of bis(benzoic acids) with bridging groups (X) that can form intramolecular hydrogen-bonds with the carboxylic acid groups, thereby controlling their conformations and thus the overall supramolecular motif.

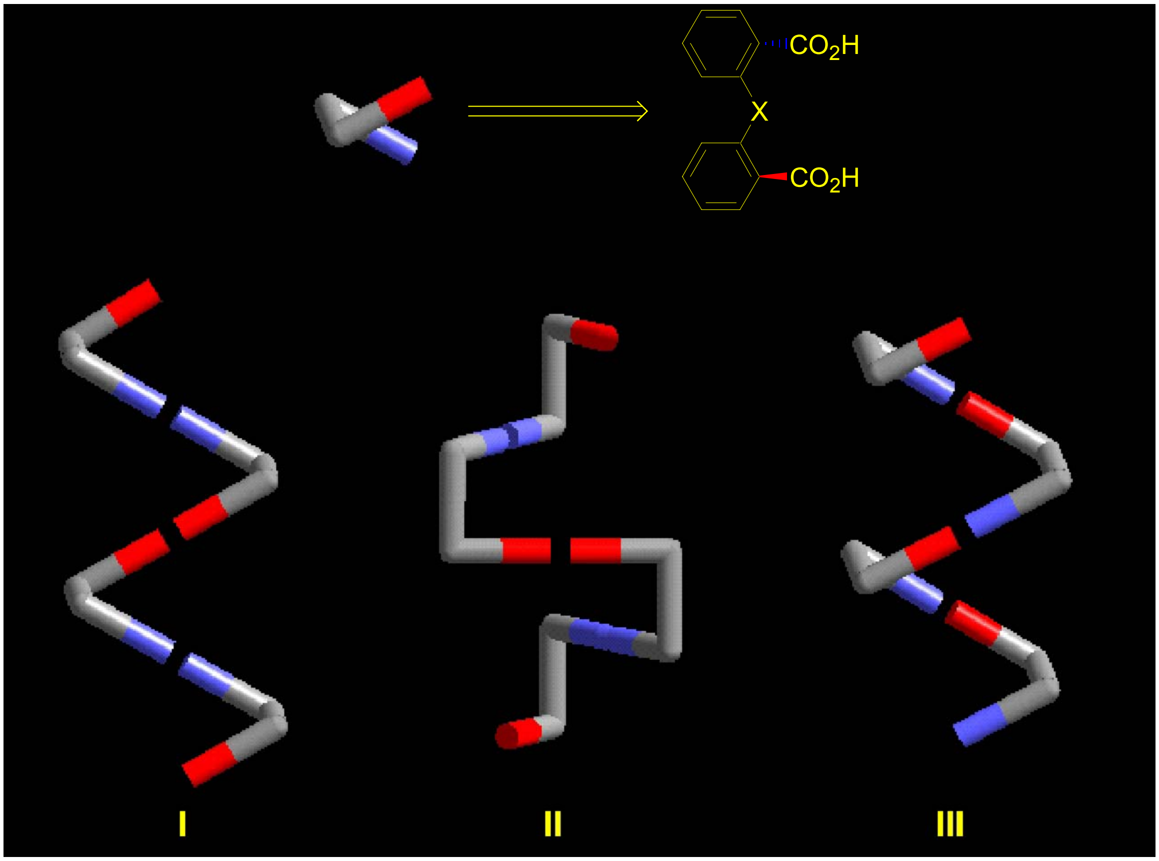


Figure 50. The three possible packing motifs of a bridged bis(benzoic acid) system. X = bridging group. Motif I is racemic, motif II and III are composed of a single atropisomer.

To test our ability to control the carboxylic acid conformation, we synthesized **42** using a copper-catalyzed ether coupling of *o*-methylphenol and *o*-iodotoluene, previously reported by our group,[41] followed by oxidation with $KMnO_4$ (Figure 51).[42] We hypothesized that the ether linkage would hydrogen-bond with one of the acidic hydrogens, resulting in the asymmetric conformation. Unfortunately, single crystal X-ray diffraction of **42** (Figure 53b) reveals that both carbonyls face away from the bridging ether, resulting in a similar zig-zag structure as seen in **41** except the conformation of the carboxylic acids are completely reversed. Such a conformation should be highly unfavourable due to the close proximity of three electronegative oxygen atoms. We hypothesize that the carboxyl hydrogens are slightly disordered such that one occupies the three-oxygen cavity for some percentage of time in the solid-state (Figure 52), thus providing stabilization for this conformation.[43]

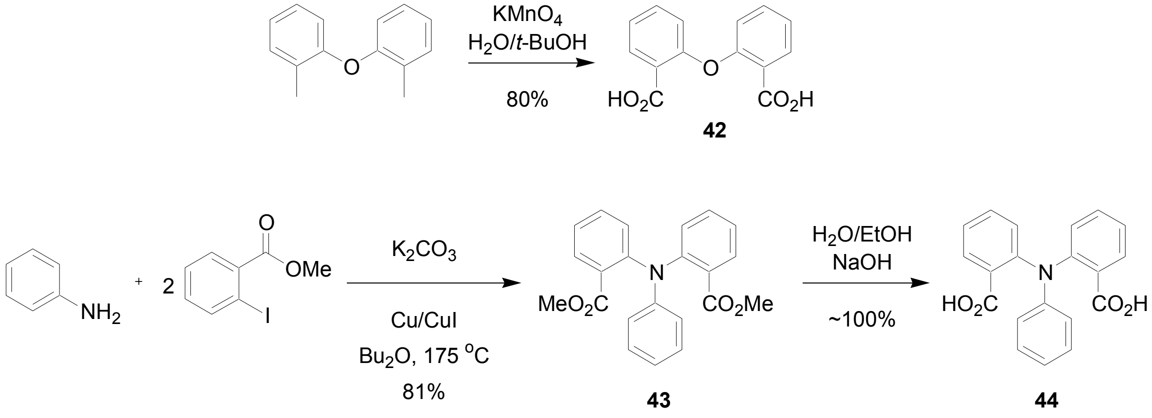
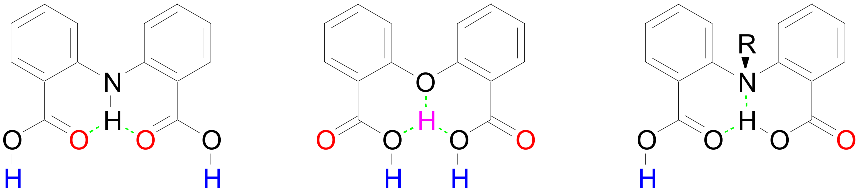


Figure 51. Syntheses of **42** and **44**.

In order to achieve the desired asymmetric conformation, we synthesized **43** through an Ullmann coupling followed by simple base hydrolysis and recrystallization from a water/acetone mixture to give **44** (Figure 51). Single crystal X-ray diffraction shows that **44** adopts an asymmetric conformation, except that the intermolecular hydrogen bonds are not dimeric. This is due to the internal hydrogen bonds between the two carboxylic acids as well as the tertiary amine (Figure 52). Moreover, **43** is observed to self-assemble into a supramolecular helix (Figure 53c) as predicted by packing motif III. It should be noted that both the right-handed and left-handed helices are present in the unit cell. It is also important to note that solvent water does not interfere in the assembly of this helical structure, a common problem in supramolecular chemistry due to competition by the protic solvent for hydrogen bonds.[3, 44, 45]



41 **42** **44**

Figure 52. The control of carboxylic acid conformations of **41**, **42**, and **44** (R=Phenyl) by internal hydrogen-bonding (green dashed). Intermolecular hydrogen-bond donors (blue) and acceptors (red); disordered hydrogen (magenta).

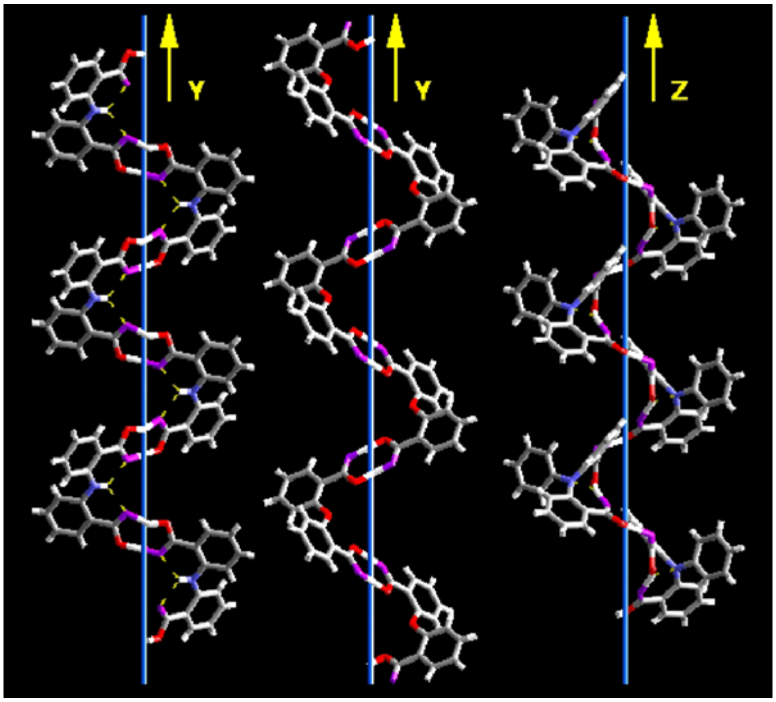


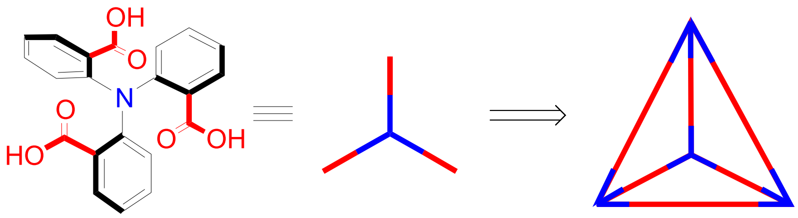
Figure 53. The supramolecular structures of a) **41**, b) **42**, and c) **44** from single crystal X-ray diffraction. Carboxylic hydrogen bonds are connected for clarity. Internal hydrogen bonds (yellow dashed lines); oxygen (red), carbonyl oxygen (purple), nitrogen (blue), carbon (grey), hydrogen (white), imaginary axis (light blue) parallel to the specified crystallographic axis.

Motif II is predicted to be less favoured due to inefficient inter-stack packing and it also forms a less efficient coil (more residues per length) than motif III. More difficult to explain is the absence of the zig-zag motif (I), which facilitates packing between stacks. The angle between the planes of the two benzoic acid rings are approximately 44°, 66°, and 81° corresponding to compounds **41**, **42**, and **44**, respectively. The more open angle of **44**, combined with its bonding conformation, may give rise to the helical assembly over the zig-zag structure. It is also possible that the bulk of the additional phenyl group in **44** is better accommodated by the helical motif in this case.

Thus, we have observed a non-chiral molecule that can form a hydrogen-bonded, crystalline, supramolecular helix. Furthermore, the conformation of the intermolecular hydrogen-bonds, and thus the overall structure, can be controlled through an intramolecular hydrogen-bond interaction.

4.3 A Discrete Hydrogen-Bonded Tetrahedron:

The assembly of molecular components into discrete regular (Platonic) and semiregular (Archimedean) polyhedra via supramolecular interactions has received substantial attention in recent years.[17-24] The interest in this area stems mainly from the desire to rationalize and mimic various naturally occurring discrete high-symmetry structures such as those found in viruses and in proteins.[46] Furthermore, since these structures have cavities that can encapsulate guest molecules, applications such as catalysis and drug delivery have also been envisaged.[8] A review of supramolecular systems based on polyhedral structures has recently been published by Atwood.[47] The tetrahedron, with four vertices and six edges, belongs to a family of five regular polyhedra collectively called the Platonic solids. In 1975, Lehn and Graf reported a macrotricyclic host that was the first covalent rendition of a tetrahedron.[48] Subsequently, several examples have appeared in the literature that use metal-ligand coordination bonds to assemble molecules into a tetrahedron.[49-52] However, we found that the clathrate compounds of quinol[53] and triphenylmethanol[54,55] were the only examples that exist for the assembly of a tetrahedron through hydrogen-bonds. Thus, we explored the triphenylamine *ortho*-tricarboxylic acid **10** (Figure 54) as a supramolecular synthon for a hydrogen bonded tetrahedron.



10

Figure 54. Schematic representation of **10** as a tetrahedral synthon.

The methyl ester derivative of **10** (i.e. R=CO_2Me) can be synthesized by the copper-catalyzed Ullmann-coupling of methyl anthranilate and methyl 2-iodobenzoate (see Chapter 2).[56] Alternatively, this compound can be synthesized by a new methodology for amination reactions using a well-defined copper-catalyst, previously reported by our group.[57] Once synthesized, the tri-*ortho*-phenylester can be easily hydrolyzed with sodium hydroxide in a water/ethanol solution to give **10** in almost quantitative yield. Recrystallization from a solution of ethanol/water gave small, but well-defined, colorless cubic crystals in 62% yield. Concentration of the filtrate and subsequent recrystallization gave a second crop of crystals for an overall yield of 93%.

Single crystal X-ray diffraction shows that **10** assemblies into tetrahedral clusters (Figure 55). These clusters are held together by hydrogen bonding interactions, however, it is not the usual dimeric interaction commonly observed for carboxylic acid moieties.[2,34] Instead, the acid groups are partially bonded to each other and partially bonded to a 3-fold disordered ethanol molecule that is present in the center of each face of the tetrahedral cluster. The secondary carbon of each ethanol molecule lies on the 3-fold symmetry axis. When connected, these carbons form a second tetrahedron within the larger tetrahedron, but with opposite geometry.[58] Both of the tetrahedral clusters have the typical dimensions of a perfect tetrahedron, namely 60° inner angles. However, the angles between the carbon-nitrogen bonds of the triarylamines occupying the vertices of the outer cluster are 118°, which deviates from the ideal tetrahedral angles of 109.5° but are consistent with the carbon-nitrogen-carbon bond angles of 120° observed for triphenylamine. The sides of the outer and inner clusters are 9.7 Å and 4.4 Å, respectively.

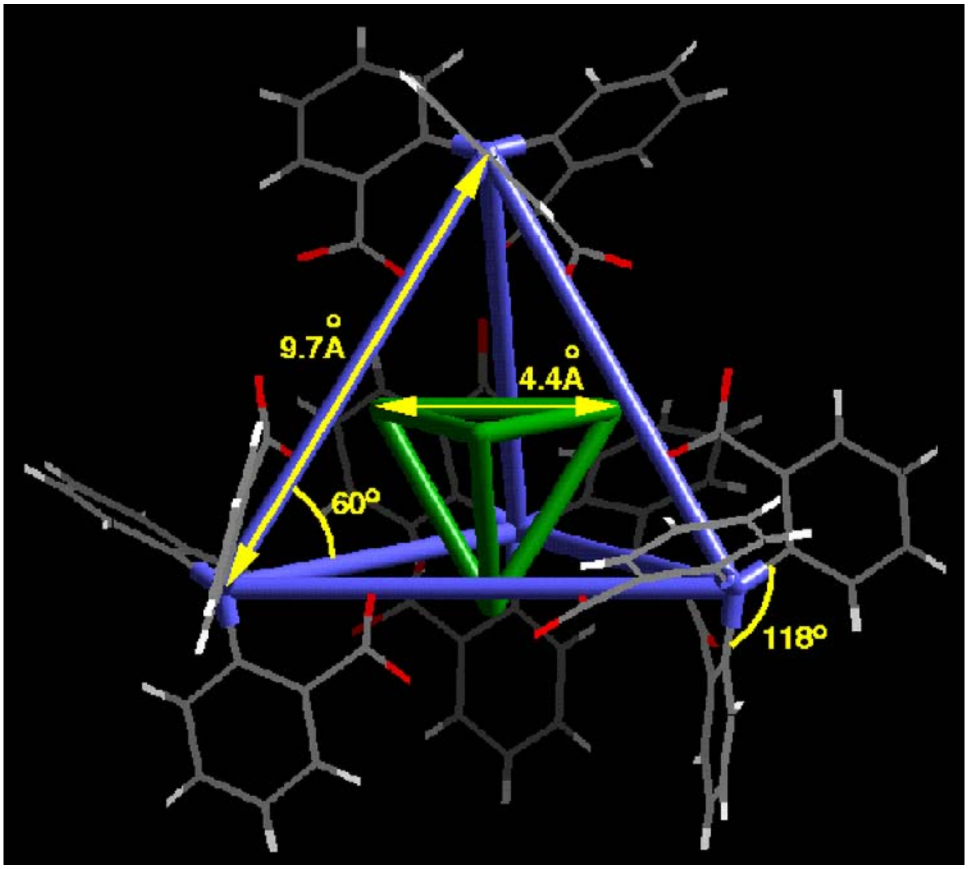


Figure 55. Illustration of the supramolecular structure of **10** from single crystal X-ray diffraction. Nitrogen atoms (blue) and the secondary carbons of the ethanol molecules (green) are connected to show the tetrahedral cluster and solvent ordering. The disordered hydrogen-bonded atoms have been removed for clarity.

Although there are no further hydrogen bond interactions between these tetrahedral clusters, they do self-organize to form a secondary structure, namely a cubic packing motif. Figure 56 shows that the tetrahedra pack in a motif that is geometrically body-centered cubic (bcc) with each side of the cube being 15.8 Å in length. Symmetrically, the packing would be more accurately described as two interpenetrated simple cubes. Although common for inorganic systems, cubic space-groups are relatively unusual for purely organic systems. In fact, a search of the Cambridge Structural Database shows that less than 0.1% of all the reported organic compounds there are cubic. This crystal structure was reproducible over multiple recrystallizations. Attempts to incorporate larger alcohols, like iso-propanol, resulted in open structures.

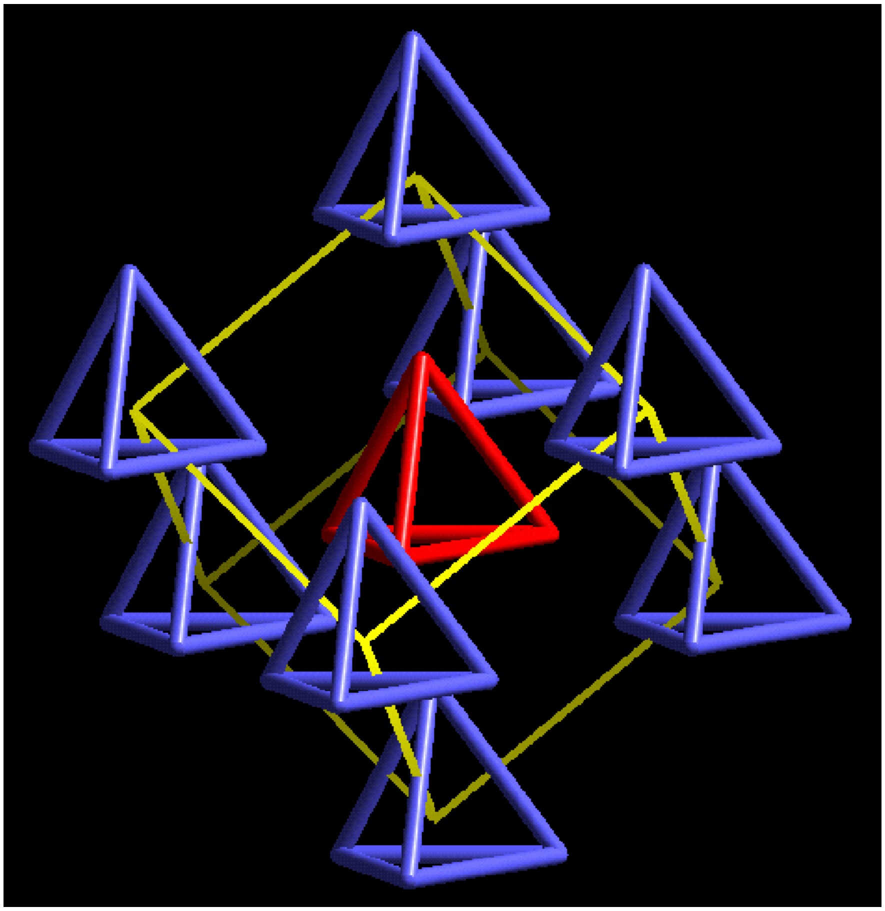


Figure 56. Illustration of the bcc-like packing motif of the supramolecular tetrahedra of **10** from single crystal X-ray diffraction. The center tetrahedron (red) is surrounded by 8 other tetrahedra (blue) that occupy the corners of the body-centered cube (yellow).

Having established the tetrahedral hydrogen-bonded structure in the solid-state, we decided to investigate the stability of this species in solution. Electrospray ionization mass spectrometry (ESI-MS) has been previously used to characterize similar stable non-covalent aggregates in solution.[59, 60] Figure 57 shows the ESI mass spectrum of **10** in a solution of 20% water in ethanol. As can be seen, the peak at *m/z* 1531.6 is predominant and corresponds to an $[M_4+Na]^+$ aggregate, presumably the tetrahedral cluster. This is an indication of the intrinsic stability of the tetrahedral structure. Also present in small amounts are peaks at *m/z* 399.9 and 1155.1 corresponding to $[M+Na]^+$ and the doubly-charged $[M_6+2Na]^{2+}$, respectively. It is also interesting to note that solutions of **10** in pure ethanol show predominately the molecular ion peak, even though the solid-state structure shows no evidence of water participating in the hydrogen-bonded structure. Water concentrations above 20% gave cluttered spectra with additional peaks corresponding to M_2 and M_3 aggregates as well as M_4 aggregate peaks with incorporated water molecules.

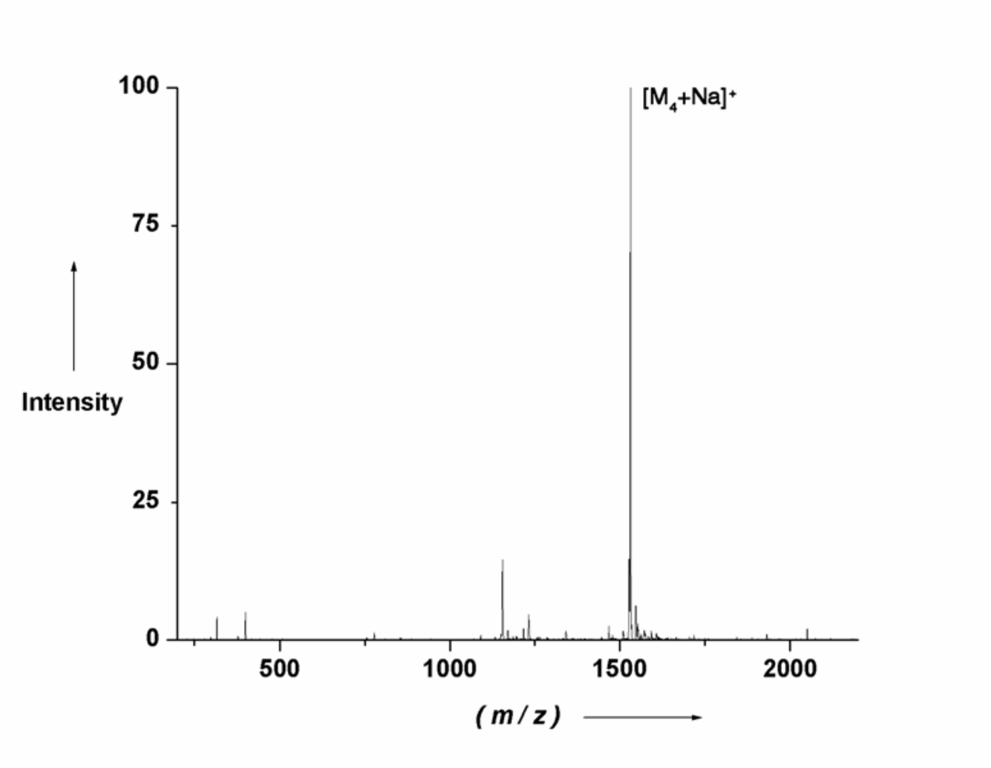


Figure 57. The electrospray ionization (ESI) mass spectrum of **10** in a 1:5 water/ethanol solution. The peak at m/z 1531.6 corresponds to the [M$_4$+Na]$^+$ aggregate.

This rare example of a discrete, fully organic, hydrogen-bonded supramolecular tetrahedron may also be of interest from a materials standpoint. The fact that there is evidence of solution structure may make this type of system interesting of molecular encapsulation applications. Also, the triarylamine constituents may provide a route to interesting electronic materials upon oxidation.

4.4 Porous Organic Networks:

The use of organic molecules as building blocks for extended frameworks has many advantages over its inorganic counterparts. The biggest advantage is the ease in which organic molecules can be modified and tailored, thus allowing for the design of unique materials with a variety of structures and properties. There has been much effort devoted to combining the flexibility of organic systems with the strength and directionality of inorganic systems.[22,25-28] By using organic ligands with specific symmetry and metals with well-defined coordination geometries, chemists have designed numerous metal-organic systems with a variety of structures.[19,20,50,51] This type of supramolecular chemistry has many names, including "self-assembly",[3,10,15,18,52,60-62] "modular chemistry",[27] and "molecular paneling",[21] however, the basic approach remains the same in all cases. The types of structures assembled in this fashion vary from discrete geometric polygons and polyhedra[18,22,23] to extended 2- or 3-dimensional networks. One of the most interesting and difficult challenges in this field is the design of a stable, porous organic network.[22, 25-30] Such a system could eventually lead to zeolite-like materials with custom designed pores. A material like this may have a variety of potential applications in catalysis, purification, and even chemical sensors. One of the most common motifs in supramolecular chemistry is that of the 3-connected net (see Chapter 2) which can be easily assembled using a supramolecular synthon with three-fold symmetry, such as trimesic acid (Figure 58a). What makes designing a porous structure difficult is the Kitaigorodski principle. This principle states that molecules prefer close packing and thus the molecules will always try to find a way to pack so as to fill any open space. With extended networks, this phenomenon is usually evident as interpenetration,[26] in which one network is linked through a second network. In trimesic acid, the 3-connected network is interpenetrated by a total of three additional nets (Figure 58b-d). Although this process results in a more robust structure, the porosity is usually lost.

We postulated that if the building block was an electroactive molecule, we may be able to create a networked electronic solid with interesting properties. Thus, we set out to synthesize the triarylamine **46** as an electroactive, three-fold symmetric building block for a 3-connected network (Figure 59).

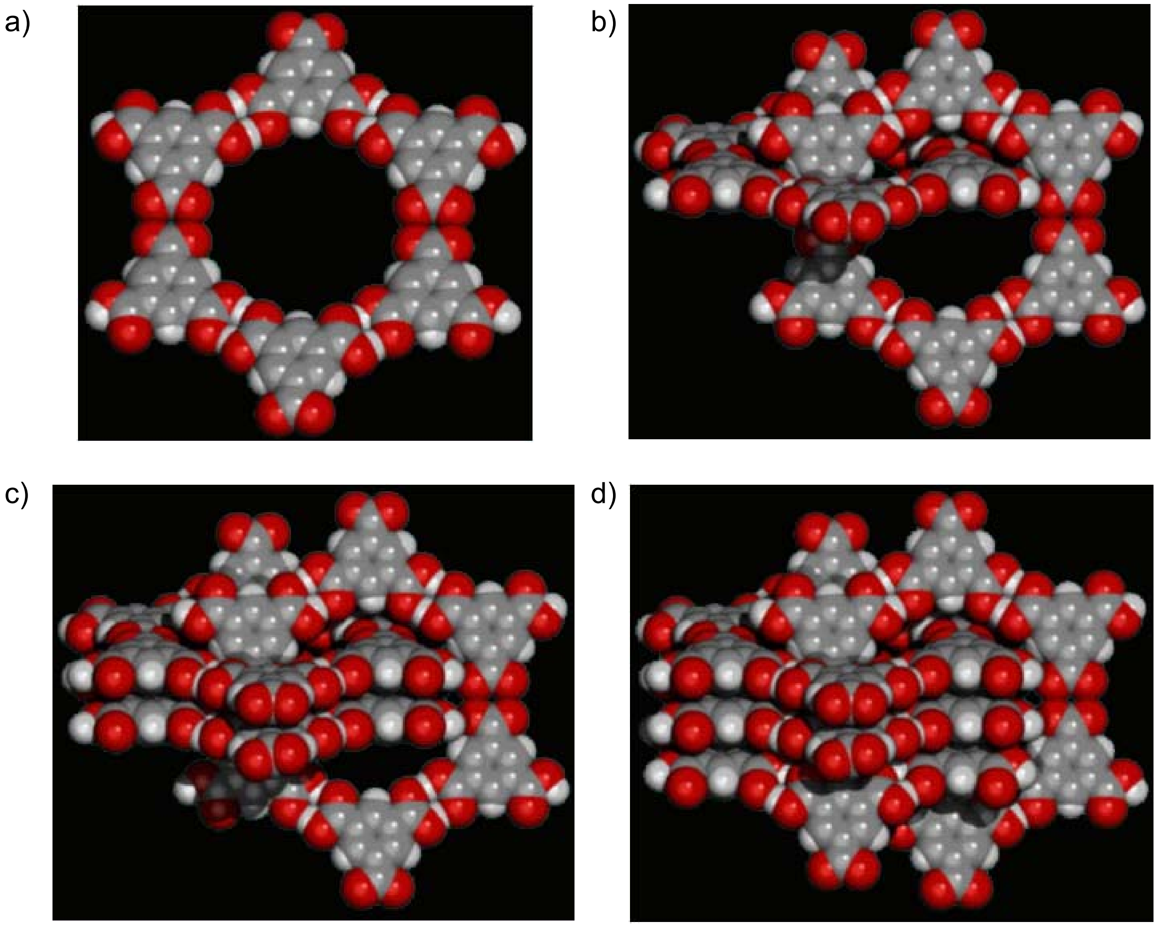


Figure 58. Trimesic acid as a building block for a 3-connected network. a) a single net; b) first interpenetration; c) second interpenetration and; d) third interpenetration.

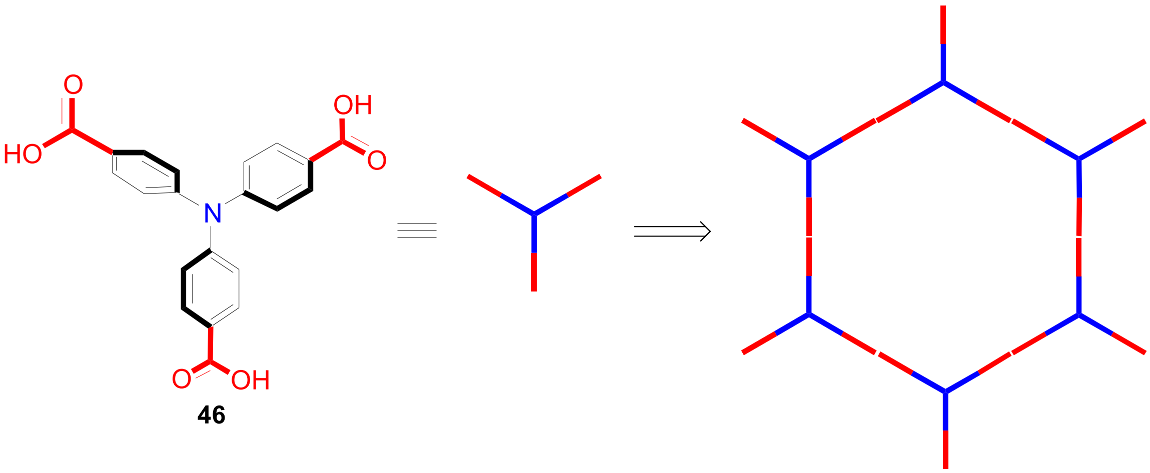


Figure 59. Triarylamine **46** as a supramolecular synthon for an electroactive 3-connected network.

The synthesis of **46** was achieved through the Hartwig[63,64]/Buchwald[65,66]-type palladium-catalyzed coupling of methyl 4-aminobenzoate and methyl 4-iodobenzoate to give **45** in 76% yield (Figure 60). Subsequent base hydrolysis gave **46** in 98% yield.

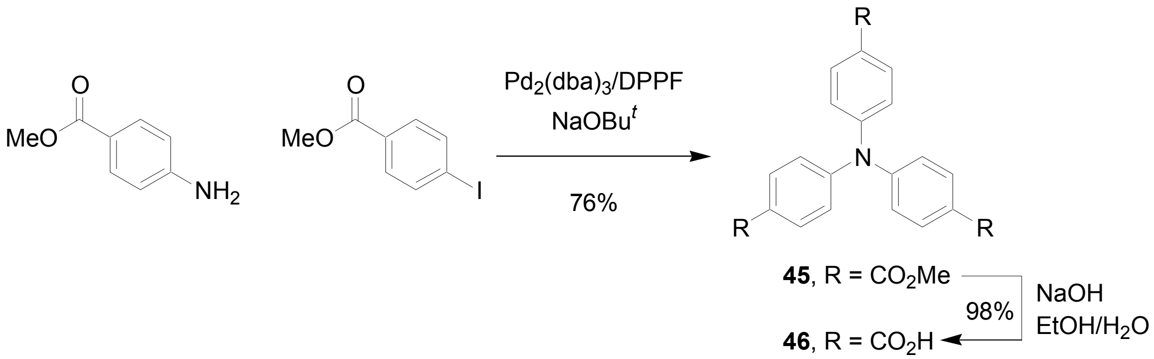


Figure 60. Synthesis of triarylamine **46**.

Recrystallization from ethanol/water in the presence of DMAP gave large crystals suitable for single crystal X-ray diffraction (Figure 61). The crystal structure shows that **46** forms undulating 3-connected nets. Each net is interpenetrated by three neighboring networks however; the structure remains porous down one axis. These pores are 7.5 Å in diameter and are occupied by DMAP molecules. This combination of interpenetration and porosity is ideal for organic porous materials which usually suffer from an inherent lack of structural integrity.

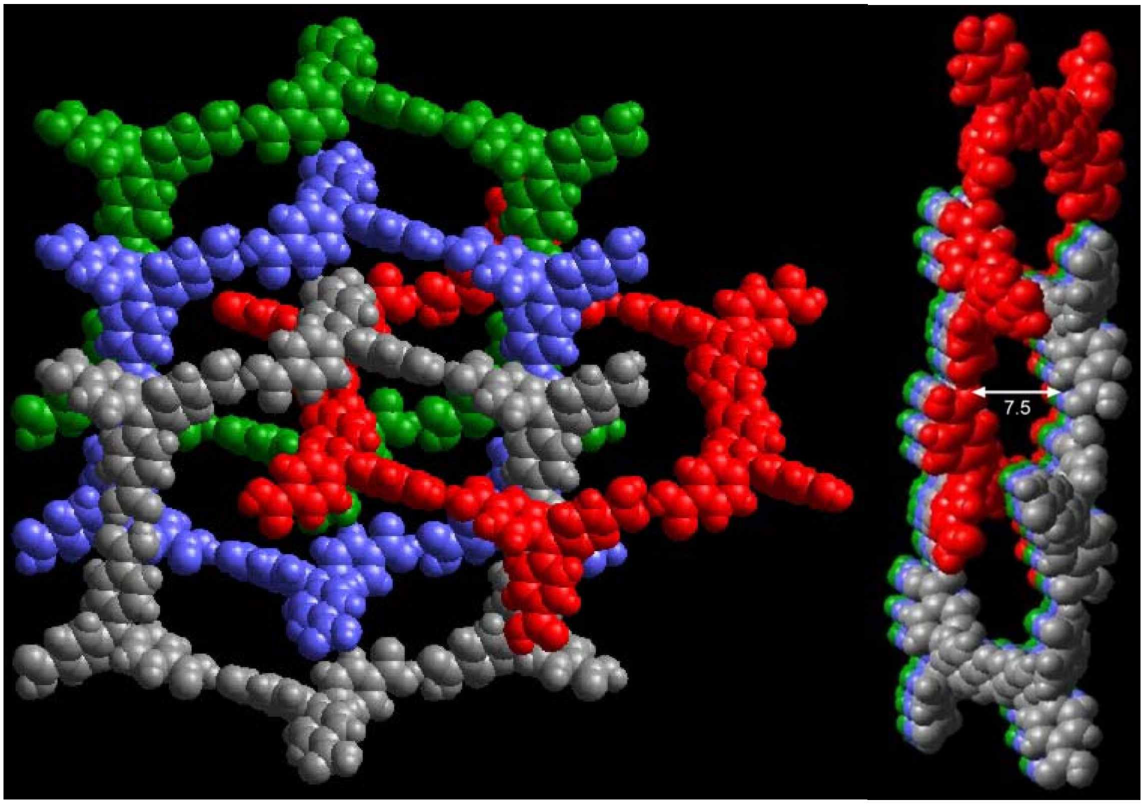


Figure 61. The X-ray crystal structure of triarylamine **46** showing the interpenetrated nets (left) and the pores (right). DMAP molecules have been removed for ease of viewing.

In order to be of practical use, a porous material must be able to exhibit sorption and desorption properties.[29, 30] This requires a tremendously robust framework. We thus attempted to crystallize **46** with various metals in the hopes that ligation of the carboxylic acids would give a stronger framework than the simple hydrogen-bonded system. Figure 62 shows the crystal structure of **46** ligated to zinc. The molecules again form 3-connected nets but with only three constituent triarylamines instead of six. These three triarylamines are coordinated to three tetrahedral zinc centers which also serve to connect them to an adjacent network. This adjacent net is close-packed with respect to the first net, thus occupying the pore created by the net. These dimers of networks are layer directly on top of each other, giving rise to a small pore of 6.7 Å. Surprisingly, the crystals of the metal-organic framework collapse within hours at room-temperature.

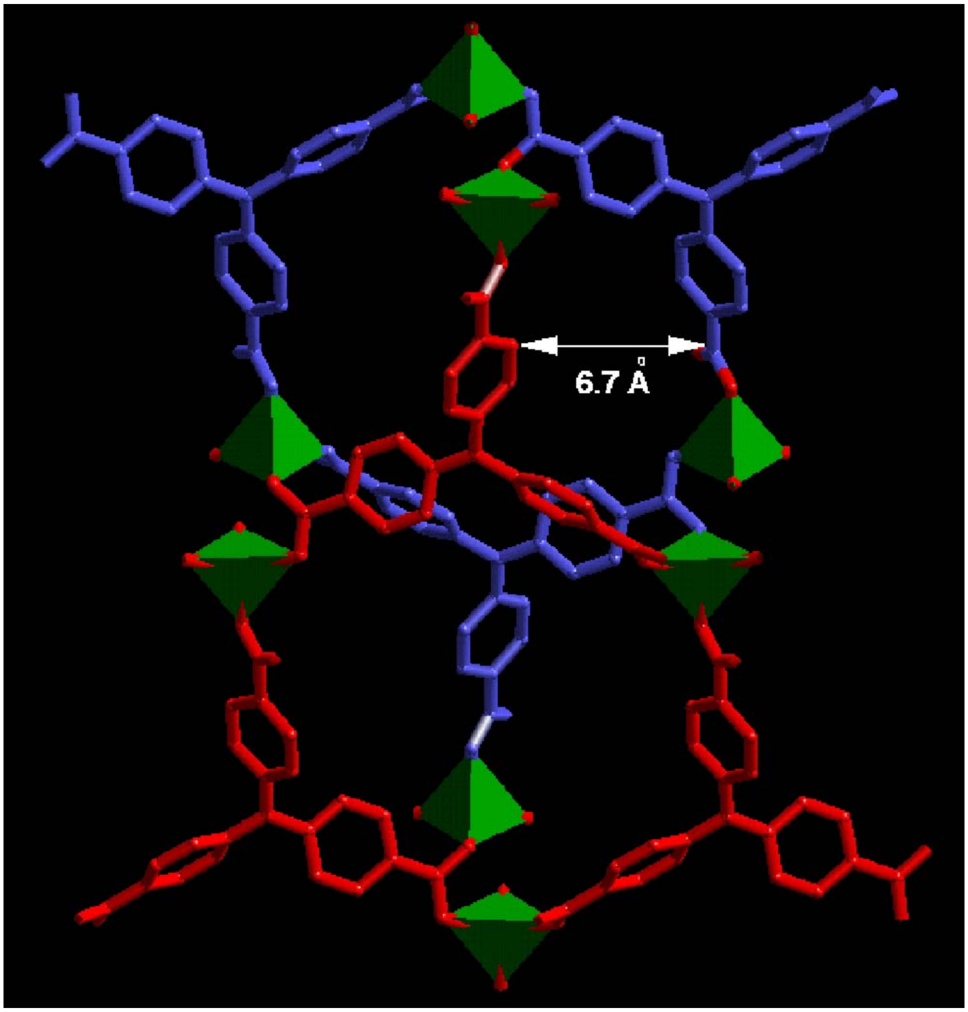


Figure 62. The X-ray crystal structure of triarylamine **46** ligated to zinc. The two dimeric networks (blue and red) are connected by tetrahedral zinc centers (green). Solvent molecules have been removed for clarity.

We also made several attempts to oxidize the triarylamine backbone to the radical cation, both prior to and after crystallization but without success. Such a system could potentially have very interesting electronic properties that may possibly be tuned depending on the nature of the guests inside the pores.

The synthetic versatility of triarylamines loan themselves well to supramolecular design and alternative networks/motifs may be constructed with these systems. The challenge remains to create an architecture with these systems that is robust enough for further manipulations (sorption or oxidation) in order to obtain a functional material.

4.5 Conclusion:

In this chapter, we have reported a novel molecular system in which the conformation of the intermolecular hydrogen-bonding, and thus the supramolecular structure, can be controlled through an internal hydrogen-bond. In this manner, zig-zag and helical topologies can be obtained from a rational design approach that may potentially lead to interesting biomimetic or electronic materials.

We have also reported a purely organic, hydrogen-bonded, supramolecular tetrahedral structure based on molecule **10**. Moreover, the ethanol solvent molecules are intrinsically ordered in a tetrahedral fashion within this structure. It may be possible to exploit the structural characteristics of this system in order to assemble new molecular encapsulation materials.

Finally, we have reported the assembly of a 3-connected, interpenetrated yet porous network based on triarylamine **46**. This electroactive porous structure may allow for interesting sensor systems in which the electronic properties of the framework are dependent on the guest molecules.

In all of these systems we have demonstrated the ability to direct the supramolecular architectures of these electroactive building blocks. These and other topologies may allow for the development of interesting electronic materials through a rational design approach of the bulk ordering down to the molecular structure. The electroactive nature and solid state properties of the triphenylamine moiety[31,32] may also assist in the development of such materials.

4.6 References:

(1) Lawrence, D. S.; Jiang, T.; Levett, M. "Self-Assembling Supramolecular Complexes" *Chem. Rev.* **1995**, *95*, 2229-2260.

(2) Desiraju, G. R. "Supramolecular Synthons in Crystal Engineering - a New Organic- Synthesis" *Angew. Chem. Int. Ed.* **1995**, *34*, 2311-2327.

(3) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. "Molecular Self-Assembly and Nanochemistry - a Chemical Strategy for the Synthesis of Nanostructures" *Science* **1991**, *254*, 1312-1319.

(4) Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. "From molecules to materials: Current trends and future directions" *Adv. Mater.* **1998**, *10*, 1297-1336.

(5) Urry, D. W. "Molecular Machines - How Motion and Other Functions of Living Organisms Can Result from Reversible Chemical-Changes" *Angew. Chem. Int. Ed.* **1993**, *32*, 819-841.

(6) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. "Functionalized pentacene: Improved electronic properties from control of solid-state order" *J. Am. Chem. Soc.* **2001**, *123*, 9482-9483.

(7) Bushey, M. L.; Hwang, A.; Stephens, P. W.; Nuckolls, C. "Enforced stacking in crowded arenes" *J. Am. Chem. Soc.* **2001**, *123*, 8157-8158.

(8) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J. "Molecular encapsulation" *Angew. Chem. Int. Ed.* **2002**, *41*, 1488-1508.

(9) Nuckolls, C.; Katz, T. J.; Katz, G.; Collings, P. J.; Castellanos, L. "Synthesis and aggregation of a conjugated helical molecule" *J. Am. Chem. Soc.* **1999**, *121*, 79-88.

(10) Norsten, T. B.; McDonald, R.; Brenda, N. R. "The self-assembly and spontaneous resolution of a hydrogen- bonded helix" *Chem. Commun.* **1999**, 719-720.

(11) Gangopadhyay, P.; Radhakrishnan, T. P. "Helical superstructures of a C-2-symmetric molecule exhibiting strong second harmonic generation in the solid-state" *Angew. Chem. Int. Ed.* **2001**, *40*, 2451-2455.

(12) Geib, S. J.; Vicent, C.; Fan, E.; Hamilton, A. D. "A Self-Assembling, Hydrogen-Bonded Helix" *Angew. Chem. Int. Ed.* **1993**, *32*, 119-121.

(13) Marsella, M. J.; Kim, I. T.; Tham, F. "Toward conjugated double helical ladder polymers: Cyclooctatetrathiophene as a highly versatile double helical scaffold" *J. Am. Chem. Soc.* **2000**, *122*, 974-975.

(14) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. "Prominent gelation and chiral aggregation of alkylamides derived from trans-1,2-diaminocyclohexane" *Angew. Chem. Int. Ed.* **1996**, *35*, 1949-1951.

(15) Hanessian, S.; Simard, M.; Roelens, S. "Molecular Recognition and Self-Assembly by Non-Amidic Hydrogen- Bonding - an Exceptional Assembler of Neutral and Charged Supramolecular Structures" *J. Am. Chem. Soc.* **1995**, *117*, 7630-7645.

(16) Jung, O. S.; Kim, Y. J.; Lee, Y. A.; Park, J. K.; Chae, H. K. "Smart molecular helical springs as tunable receptors" *J. Am. Chem. Soc.* **2000**, *122*, 9921-9925.

(17) MacGillivray, L. R.; Atwood, J. L. "Cavity-containing materials based upon resorcin 4 arenes by discovery and design" *J. Solid State Chem.* **2000**, *152*, 199-210.

(18) Stang, P. J.; Olenyuk, B. "Self-assembly, symmetry, and molecular architecture: Coordination as the motif in the rational design of supramolecular metallacyclic polygons and polyhedra" *Acc. Chem. Res.* **1997**, *30*, 502-518.

(19) Caulder, D. L.; Raymond, K. N. "The rational design of high symmetry coordination clusters" *J. Chem. Soc. Dalton Trans.* **1999**, 1185-1200.

(20) Caulder, D. L.; Raymond, K. N. "Supermolecules by design" *Acc. Chem. Res.* **1999**, *32*, 975-982.

(21) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. "Molecular paneling via coordination" *Chem. Commun.* **2001**, 509-518.

(22) Lu, J. J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. "Polygons and faceted polyhedra and nanoporous networks" *Angew. Chem. Int. Ed.* **2001**, *40*, 2113-2116.

(23) Moulton, B.; Lu, J. J.; Mondal, A.; Zaworotko, M. J. "Nanoballs: nanoscale faceted polyhedra with large windows and cavities" *Chem. Commun.* **2001**, 863-864.

(24) MacGillivray, L. R.; Atwood, J. L. "A chiral spherical molecular assembly held together by 60 hydrogen bonds" *Nature* **1997**, *389*, 469-472.

(25) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. "Infinite secondary building units and forbidden catenation in metal-organic frameworks" *Angewandte Chemie-International Edition* **2001**, *41*, 284-+.

(26) Chen, B. L.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. "Interwoven metal-organic framework on a periodic minimal surface with extra-large pores" *Science* **2001**, *291*, 1021-1023.

(27) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. "Modular chemistry: Secondary building units as a basis for the

design of highly porous and robust metal-organic carboxylate frameworks" *Acc. Chem. Res.* **2001**, *34*, 319-330.

(28) Kim, J.; Chen, B. L.; Reineke, T. M.; Li, H. L.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. "Assembly of metal-organic frameworks from large organic and inorganic secondary building units: New examples and simplifying principles for complex structures" *J. Am. Chem. Soc.* **2001**, *123*, 8239-8247.

(29) Yaghi, O. M.; Li, H. L.; Davis, C.; Richardson, D.; Groy, T. L. "Synthetic strategies, structure patterns, and emerging properties in the chemistry of modular porous solids" *Acc. Chem. Res.* **1998**, *31*, 474-484.

(30) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. "Tailored porous materials" *Chem. Mater.* **1999**, *11*, 2633-2656.

(31) Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. "New triarylamine-containing polymers as hole transport materials in organic light-emitting diodes: Effect of polymer structure and cross-linking on device characteristics" *Chem. Mater.* **1998**, *10*, 1668-1676.

(32) Shirota, Y. "Organic materials for electronic and optoelectronic devices" *J. Mater. Chem.* **2000**, *10*, 1-25.

(33) Rowan, A. E.; Nolte, R. J. M. "Helical molecular programming" *Angew. Chem. Int. Ed.* **1998**, *37*, 63-68.

(34) Leiserowitz, L. "Molecular Packing Modes. Carboxylic Acids" *Acta Crystallogr. Sect. B* **1976**, *32*, 775-802.

(35) Bilton, C.; Allen, F. H.; Shields, G. P.; Howard, J. A. K. "Intramolecular hydrogen bonds: common motifs, probabilities of formation and implications for supramolecular organization" *Acta Crystallogr. Sect. B* **2000**, *56*, 849-856.

(36) Ducharme, Y.; Wuest, J. D. "Use of Hydrogen-Bonds to Control Molecular Aggregation - Extensive, Self-Complementary Arrays of Donors and Acceptors" *J. Org. Chem.* **1988**, *53*, 5787-5789.

(37) Boucher, E.; Simard, M.; Wuest, J. D. "Use of Hydrogen-Bonds to Control Molecular Aggregation - Behavior of Dipyridones and Pyridone-Pyrimidones Designed to Form Cyclic Triplexes" *J. Org. Chem.* **1995**, *60*, 1408-1412.

(38) Vaillancourt, L.; Simard, M.; Wuest, J. D. "Synthesis and self-association of 4-pyrimidinones" *J. Org. Chem.* **1998**, *63*, 9746-9752.

(39) Zhu, J.; Parra, R. D.; Zeng, H. Q.; Skrzypczak-Jankun, E.; Zeng, X. C.; Gong, B. "A new class of folding oligomers: Crescent oligoamides" *J. Am. Chem. Soc.* **2000**, *122*, 4219-4220.

(40) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. "Novel folding patterns in a family of oligoanthranilamides: Non-peptide oligomers that form extended helical secondary structures" *J. Am. Chem. Soc.* **1997**, *119*, 10587-10593.

(41) Gujadhur, R.; Venkataraman, D. "Synthesis of diaryl ethers using an easy-to-prepare, air- stable, soluble copper(I) catalyst" *Synth. Commun.* **2001**, *31*, 2865-2879.

(42) Shapiro, R.; Slobodin, D. "Synthesis of the dibenzo[b,g]oxocin system" *J. Org. Chem.* **1969**, *34*, 1165-1168.

(43) Although not conclusive, X-ray diffraction shows some residual electron density where the disordered proton is expected.

(44) Desiraju, G. R. "Hydration in Organic-Crystals - Prediction from Molecular-Structure" *Chem. Commun.* **1991**, 426-428.

(45) Hirschberg, J.; Brunsveld, L.; Ramzi, A.; Vekemans, J.; Sijbesma, R. P.; Meijer, E. W. "Helical self-assembled polymers from cooperative stacking of hydrogen-bonded pairs" *Nature* **2000**, *407*, 167-170.

(46) Namba, K.; Stubbs, G. "Structure of Tobacco Mosaic-Virus at 3.6-a Resolution - Implications for Assembly" *Science* **1986**, *231*, 1401-1406.

(47) MacGillivray, L. R.; Atwood, J. L. "Structural classification and general principles for the design of spherical molecular hosts" *Angew. Chem. Int. Ed.* **1999**, *38*, 1019-1034.

(48) Graf, E.; Lehn, J. M. "Cryptates. XVII. Synthesis and cryptate complexes of a spheroidal macrotricyclic ligand with octahedrotetrahedral coordination" *J. Am. Chem. Soc.* **1975**, *97*, 5022-5024.

(49) Fox, O. D.; Drew, M. G. B.; Beer, P. D. "Resorcarene-based nanoarchitectures: Metal-directed assembly of a molecular loop and tetrahedron" *Angew. Chem. Int. Ed.* **2000**, *39*, 135-140.

(50) Terpin, A. J.; Ziegler, M.; Johnson, D. W.; Raymond, K. N. "Resolution and kinetic stability of a chiral supramolecular assembly made of labile components" *Angew. Chem. Int. Ed.* **2001**, *40*, 157-160.

(51) Bruckner, C.; Powers, R. E.; Raymond, K. N. "Symmetry-driven rational design of a tetrahedral supramolecular Ti4L4 cluster" *Angew. Chem. Int. Ed.* **1998**, *37*, 1837-1839.

(52) Paul, R. L.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Reeves, Z. R.; Ward, M. D. "Effects of metal co-ordination geometry on self-assembly: a dinuclear double helicate complex and a tetranuclear cage complex of a new bis-bidentate bridging ligand" *J. Chem. Soc. Dalton Trans.* **2000**, 845-851.

(53) Ermer, O.; Robke, C. "New Host Architecture of Hydroquinone with Enclathrated C-70" *J. Am. Chem. Soc.* **1993**, *115*, 10077-10082.

(54) Ferguson, G.; Gallagher, J. F.; Glidewell, C.; Low, J. N.; Scrimgeour, S. N. "The Structure of Triphenylmethanol, Ph3coh" *Acta Crystallogr. Sect. C* **1992**, *48*, 1272-1275.

(55) Aliev, A. E.; MacLean, E. J.; Harris, K. D. M.; Kariuki, B. M.; Glidewell, C. "Dynamics of the hydrogen-bonding arrangement in solid triphenylmethanol: An investigation by solid-state H-2 NMR spectroscopy" *J. Phys. Chem. B* **1998**, *102*, 2165-2175.

(56) Field, J. E.; Venkataraman, D. "Heterotriangulenes - Structure and properties" *Chem. Mater.* **2002**, *14*, 962-964.

(57) Gujadhur, R.; Venkataraman, D.; Kintigh, J. T. "Formation of aryl-nitrogen bonds using a soluble copper(I) catalyst" *Tetrahedron Lett.* **2001**, *42*, 4791-4793.

(58) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. "A well-resolved ice-like (H2O)(8) cluster in an organic supramolecular complex" *J. Am. Chem. Soc.* **2001**, *123*, 7192-7193.

(59) Cheng, X. H.; Gao, Q. Y.; Smith, R. D.; Simanek, E. E.; Mammen, M.; Whitesides, G. M. "Characterization of hydrogen-bonded aggregates in chloroform by electrospray ionization mass spectrometry" *J. Org. Chem.* **1996**, *61*, 2204-2206.

(60) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J. "Self-assembly of molecular prisms via an organometallic "clip"" *Org. Lett.* **2002**, *4*, 913-915.

(61) Nelson, J. "Solar energy - Solar cells by self-assembly?" *Science* **2001**, *293*, 1059-1060.

(62) Tanaka, K.; Kitahara, Y. "Self-assembly of (P)-heterohelicenediol into a four-leaf clover motif" *Chem. Commun.* **1998**, 1141-1142.

(63) Hartwig, J. F. "Carbon-heteroatom bond-forming reductive eliminations of amines, ethers, and sulfides" *Acc. Chem. Res.* **1998**, *31*, 852-860.

(64) Hartwig, J. F. "Transition metal catalyzed synthesis of arylamines and aryl ethers from aryl halides and triflates: Scope and mechanism" *Angew. Chem. Int. Ed.* **1998**, *37*, 2047-2067.

(65) Muci, A. R.; Buchwald, S. L. "Practical palladium catalysts for C-N and C-O bond formation", *Cross-Coupling Reactions, Vol. 219*, **2002**; pp 131-209.

(66) Yang, B. H.; Buchwald, S. L. "Palladium-catalyzed amination of aryl halides and sulfonates" *J. Organomet. Chem.* **1999**, *576*, 125-146.

CHAPTER 5

CONCLUSIONS

The control of molecular structure through organic synthesis has been thoroughly demonstrated throughout the literature over the past half century. The control of supramolecular structure has been called the “new organic synthesis”, as many of the strategies developed for traditional organic chemistry parallel those emerging for supramolecular chemistry. It was our intent at the outset of this research, to combine the molecular control of organic synthesis with the supramolecular control of bulk molecular ordering to make unique electronic materials. We focused our efforts on arylamines which have found wide application as electronic materials in a variety of applications. Their reputation as stable, synthetically accessible, and easily modified molecules make them an attractive building block for new electronic materials.

We have developed a new, mild synthesis of the D_{3h} triketone **3** as a building block for higher dimensional electroactive solids. The synthesis of the D_{3h} triketone **3** is an example of utilizing organic synthesis to make a molecule with the appropriate molecular symmetry to assemble in a predictable manner in the solid state. The crystal structure of this molecule demonstrates a propensity for forming columnar π-stacks that are oriented in a herring-bone type fashion with respect to one another. This planar molecule has enormous potential as a core structure for higher dimensional electronic solids and discotic phases. The challenge still facing the development of this molecule as a practical material lies in the ability to functionalize it with appropriate substituents to achieve the desired bulk structure. The mild synthesis, along with the solid state structure and characteristic properties reported here will facilitate the further development of these compounds.

Demonstrating structural control at the molecular level, we have synthesized a series of helical bridged triarylamines. We have elucidated the solid state structure, photochemical, and electrochemical properties of these unique heterohelicenes. These are the first reported helicenes that are capable of being oxidized to a radical cation. This may allow for examination of the effects of molecular helicity on bulk charge transport. We have also shown that these molecules can be separated into their chiral atropisomers using a camphanate ester as the resolving agent. These chiral helicenes are one of the few organic molecules capable of emitting circularly polarized light (CPL). The combination of the electronic and photochemical properties of these systems make them ideal for the construction of CPL emitting diodes which may be utilized as back-lighting in LCD displays. The future of these materials lies in the modification of the molecular helix in order to obtain an increased CPL response. Other applications such as non-linear optics (NLO) may also be able to utilize these types of systems.

Finally, we have demonstrated the control of the supramolecular assemblies of several arylamines to form ziz-zag, helical, tetrahedral, and porous solid state architectures. The study of supramolecular helicity versus the zig-zag structure is a beautiful example of directing solid state structure through the manipulation of weak molecular interactions. The discrete hydrogen-bonded tetrahedron is a unique structure for a fully organic supramolecular assembly, particularly in a cubic space group (very rare for organic systems). The fact that this structure is evident by electrospray ionization mass spectrometry in the solution phase is indicative that these solid state interactions may be stronger than we currently perceive. The porous organic frameworks are still relatively unstable for sorption/desorption applications. However, since the constituent building block is an electroactive triarylamine, it may be possible to utilize this porous structure for developing an interesting electronic material, such as a sensor. Further systems need to be explored in this regard.

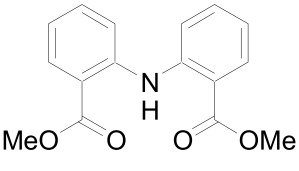
In summary, we have demonstrated control of arylamines both at the molecular and supramolecular structures in order to gain desired properties. There is great potential for use of these systems in practical device applications. However, before this is possible, further investigation at the laboratory level is required in order to obtain the maximum performance of these materials.

APPENDIX 1

EXPERIMENTAL

General Information. All chemicals were purchased from major chemical suppliers and were used without further purification. Flash chromatography was performed using ICN flash silica gel, 230-400 mesh. All ^{1}H and ^{13}C NMR spectra were recorded on a Brucker DPX300 MHz spectrometer. Chemical shifts (δ) and coupling constants (J) are reported in parts per million (relative to internal TMS) and Hertz, respectively. The abbreviations for splitting patterns are s, singlet; br s, broad singlet; d, doublet, t, triplet; q, quartet; and combinations therein (i.e. dd, doublet of doublets). Elemental analyses were performed in the Microanalysis Laboratory, University of Massachusetts at Amherst, by Dr. Greg Dabkowski. Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry Facility which is supported, in part, by the National Science Foundation. X-ray crystallographic data was obtained at the X-ray Structural Characterization Laboratory and the University of Massachusetts Mass Spectrometry Facility which is supported by the National Science Foundation grant CHE-9974648. X-ray data were collected using a Nonius kappa-CCD diffractometer with MoKα (λ=0.71072 Å) as the incident radiation. Diffraction data were collected at ambient temperature unless otherwise stated. The raw data were integrated, refined, scaled, and corrected for Lorentz polarization and absorption effects, if necessary, using the programs DENZO and SCALEPAK, supplied by Nonius. Structure solutions and refinements were done (on F_o^2) using a suite of programs such as SIR97, SIR92, LSQ, SHELXS and SHELXL that are contained within the Nonius MAXUS module. All structures were checked for any missing symmetry using MISSYM of PLATON. Cyclic voltammetry was carried out using a BAS CV-50W voltammetric analyzer with a glassy carbon working electrode, a platinum auxiliary electrode, and a silver wire pseudo reference electrode. A scan rate of

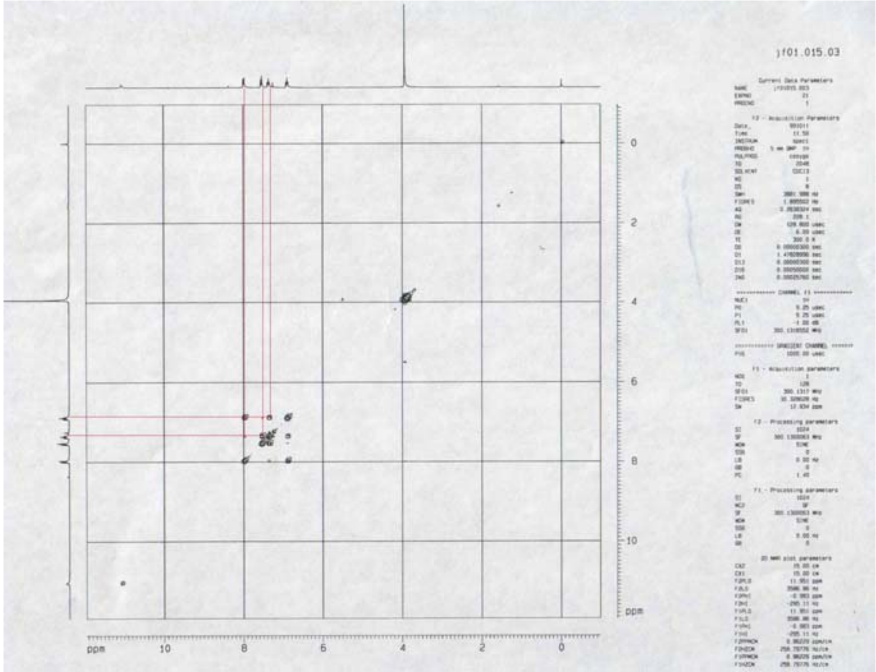
250 mV/s was employed. Ferrocene/ferrocenium was added as an internal reference. The values were then adjusted to values versus standard calomel electrode given ferrocene/ferrocenium $E_{1/2}$=0.307 V vs. SCE. All electrochemical experiments were carried out using analyte concentrations of 10^{-3} M in dichloromethane and electrolyte (tetrabutylammonium hexafluorophosphate) concentrations of 0.1 M. Air was removed from the solvent and replaced with argon through several freeze/pump/thaw cycles. UV-visible absorption spectra were collected using a Hewlett-Packard 8452A Diode Array Spectrophotometer using a 1 cm quartz cuvette. Molar absorbtivities (ε) were only calculated for signals under 1.0 Absorbance. Corresponding emission spectra were collected using a Shimadzu RF-5301 PC Spectrofluorophotometer using a 1 cm quartz cuvette. A scaling factor was applied to both absorption and emission spectra in order to place the maximum wavelength intensities on a similar scale for ease of viewing. Quantum yields were calculated using the formula $\Phi_s=\Phi_r\times(I_s/I_r)\times(A_r/A_s)$, where subscripts "s" and "r" refer to sample and reference. Φ=quantum yield (Φ_r=0.92 for perylene in benzene), I=the integrated area under the emission spectra, and A=the absorbance at the wavelength of excitation. CD was performed on a Jasco 700 Spectrophotometer, using a quartz cuvette with a 1-mm path length. Scans were taken from 230 to 500 nm at a rate of 100 nm/sec, with a 1.0 nm step resolution and a 4-s response. One scan was taken for each sample at a constant temperature of 23 °C. Data obtained with a high tension voltage over 600 V were not included in the analysis.

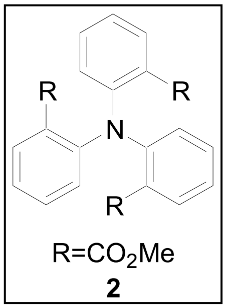


1

bis(o-methylbenzoate)amine (1). $Pd_2(dba)_3$ (0.458 g, 0.5 mmol), DPPB (0.320 g, 0.75 mmol), and methyl 2-bromobenzoate (1.68 mL, 12 mmol) were combined in a 50-mL Schlenk flask under argon. Dry toluene (20 mL) was added and the reaction mixture was stirred for 10 min. at room temperature. Methylanthranilate (1.29 mL, 10 mmol) was added followed by NaOMe (0.810 g, 15 mmol) and the reaction heated to 110 °C for 18 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated by rotary evaporation, and the resulting residue was purified by column chromatography using 2:1 ether:hexane as the eluent. Recrystallization from hexane gave 2.289 g (80% yield) of **1** as a yellow crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 6.90 (td, J = 1.3 and 7.1 Hz, 1H), 7.37 (td, *J* = 1.7 and 7.6 Hz, 1H),7.55 (dd, *J* = 1.0 and 8.49 Hz, 1H), 7.98 (dd, *J* = 1.7 and 7.9 Hz, 9H), 11.06 (bs, 1H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 52.3, 117.2, 117.7, 119.9, 131.9, 133.4, 144.3, 168.9. Anal. Calcd for $C_{16}H_{15}O_4N$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.31; H, 5.21; N, 4.83.

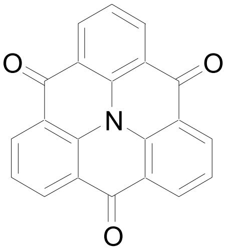
COSY NMR (300 MHz, $CDCl_3$):





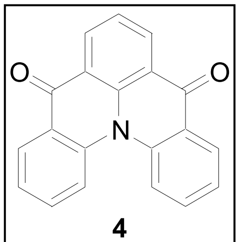
2

***o*,*o*',*o*''-amino-trisbenzoic acid-trimethylester (2).** A 100 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with methyl anthranilate (3.24 mL, 25 mmol), methyl-2-iodobenzoate (13.32 mL, 62.5 mmol), K_2CO_3 (27.64 g, 200 mmol), Copper bronze (0.508 g, 6 mmol), and 18-crown-6 (0.322 g, 5.0 mmol). 25 mL of *o*-dichlorobenzene was added and the reaction heated to reflux, under argon, for 17 h. The solvent was distilled off under reduced pressure and the residue filtered through Celite with hot ethanol and the filtrate concentrated under vacuum. The crude product was purified by column chromatography on silica gel using 3:1 hexane/ethyl acetate as the eluent, to yield 5.769 g (55% Yield) of **2**. ^1H NMR (300 MHz, $CDCl_3$): δ 7.82 (m, 3H), 7.50 (m, 3H), 7.02 (m, 6H), 3.51 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 52.0, 123.5, 126.1, 127.4, 131.0, 132.4, 146.9, 167.7. Anal. Calcd for $C_{24}H_{21}O_6N$: C, 68.73; H, 5.01; N, 3.34. Found: C, 68.25; H, 5.01; N, 3.72. Crystal data: Triclinic, *P*-1, *a* = 8.2076(8) Å, *b* = 8.8702 (8) Å, *c* = 15.687 (2) Å, *V* = 1081.1(2) Å^3, *Z* = 2, number of unique reflections = 3267, number of parameters = 280, R_1 = 0.0942 (all data), GOF = 1.067, residual electron density = +0.131 e/Å^3.



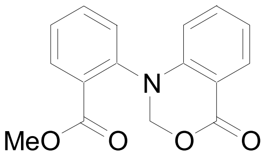
3

12c-aza-dibenzo[cd,mn]pyrene-4,8,12-trione (3). In a 250 mL round-bottom flask, equipped with a reflux condenser, *o*,*o*',*o*''-amino-trisbenzoic acid-trimethylester **2** (4.978 g, 12.0 mmol) was combined with sodium hydroxide (6.00 g, 150 mmol) in 50 mL of an ethanol/water (1:1) mixture. The reaction was heated to reflux for 3 h and then acidified with dilute hydrochloric acid to pH~2-3. The triacid precipitated as a white solid and was collected by vacuum filtration, oven dried (4.299 g, 93%) and used without further purification. The triacid (0.377 g, 1.0 mmol), $SOCl_2$ (0.66 mL, 9 mmol), and 2 drops of DMF was refluxed in 10 mL dry dichloromethane for 3 h. $SnCl_4$ (1.04 mL, 9 mmol) was added and the reaction refluxed for an additional 15 h. The reaction mixture was added dropwise to a stirring solution of aqueous NaOH and stirred for 30 min. The resulting precipitate was collected by vacuum filtration and washed with water and then ethanol and oven dried to give 0.259 g of **3** (80% yield). Fine yellow crystals of **3** can be obtained by recrystallization from nitrobenzene. ^{1}H NMR (300 MHz, 10% TFA-d in $CDCl_3$): δ 9.17 (d, *J*=7.72 Hz, 2H), 8.04 (t, *J*=7.72 Hz, 1H). ^{13}C NMR (300 MHz, 10% TFA-d in $CDCl_3$): δ 178.5, 138.3, 136.9, 127.2, 123.1. HRMS Calcd for $C_{21}H_9NO_3$: 323.0582 Found: 323.0595. Crystal data: $C_{21}H_9NO_3$, M = 323.307, Monoclinic, P 21/n, a = 3.8947(3) Å, b = 18.039(2) Å, c = 19.303(2) Å, α = 90.00°, β = 92.202(3)°, γ = 90.00°, V = 1355.2(2) Å^3, Z = 4, μ = 0.107 mm^{-1}, T = 298 K, data/parameters = 1245/226, converging to R_1 = 0.0620, wR_2 = 0.1536 (on 767, $I > 2\sigma(I)$ observed data); R_1 = 0.1194, wR_2 = 0.2082 (all data), residual electron density: 0.278 e/Å^3.



4

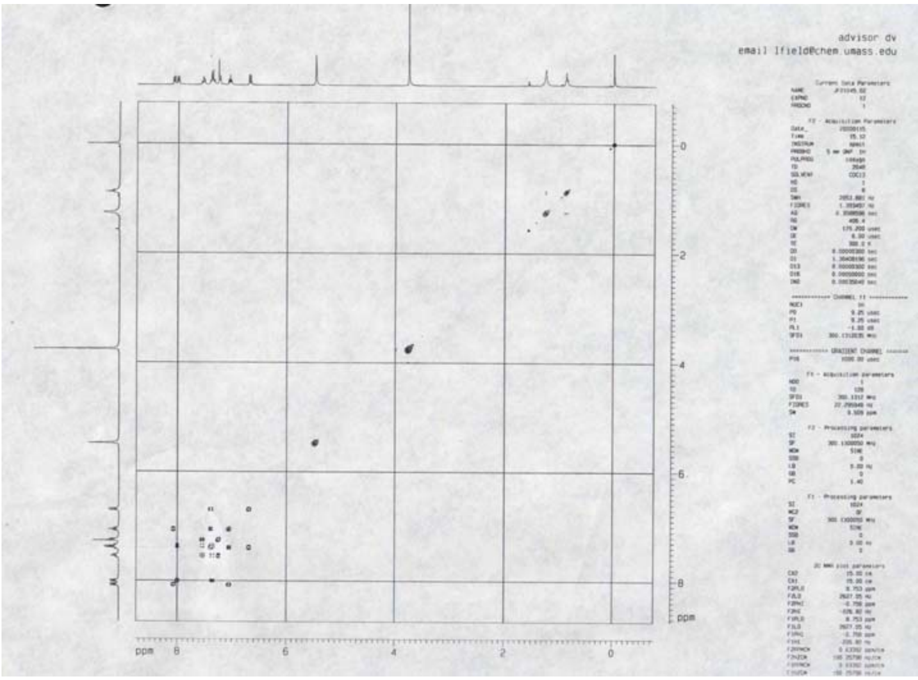
13b-aza-naphtho[3,2,1-de]anthracene-5,9-dione (4). In a 100 mL round-bottom flask equipped with a reflux condenser, N,N-bis-(2-methoxycarbonyl-phenyl)-aniline (3.610 g, 10 mmol) was combined with sodium hydroxide (2.00 g, 50 mmol) in 30 mL of an ethanol/water (1:1) mixture. The reaction was heated to reflux for 3 h and then acidified with dilute hydrochloric acid to pH~2-3. The diacid precipitated as a white solid and was collected by vacuum filtration, oven dried (3.284g, 99% yield) and used without further purification. The above hydrolyzed product (1.877 g, 5.63 mmol) was combined with 30 mL of dichloromethane and oxalyl chloride (1.47 mL, 16.89 mmol) and heated to reflux for 2 h. Iron (III) chloride (9.13 g, 56.3 mmol) was added and the reaction heated to reflux for 15 h. The reaction mixture was filtered through Celite and washed with dichloromethane. The filtrate was extracted with water/CH_2Cl_2, the organic layer dried and concentrated under vacuum. The crude material was purified by flash chromatography using a 2:1 mixture of hexane/ethyl acetate as the eluent to give 0.646 g (39% yield) of **4** as a yellow solid. The product can be recrystallized from dichloromethane layered with hexane, to give **4** as yellow cubic crystals. ^{1}H NMR: ($CDCl_3$) δ 8.73 (d, *J*=7.72 Hz, 2H), 8.49 (dd, *J*=7.91, 1.69 Hz, 2H), 8.14 (d, *J*=8.67 Hz, 2H), 7.70 (dt, *J*=7.82, 1.70 Hz, 2H), 7.65 (t, *J*=7.73 Hz, 2H), 7.49 (dt, *J*=7.63, 0.95 Hz, 2H). ^{13}C NMR: ($CDCl_3$) δ 178.8, 139.9, 139.4, 133.1, 132.9, 128.0, 126.6, 125.4, 127.7, 123.6, 120.4. Anal. Calcd for $C_{20}H_{11}NO_2$: C, 80.80; H, 3.73; N, 4.71. Found: C, 79.57; H, 3.49; N, 4.55. HRMS Calcd for $C_{20}H_{11}NO_2$: 297.0790 Found: 297.0796. Crystal data: $C_{20}H_{11}NO_2$, M = 297.313, Monoclinic, C 2/c, a = 9.2322(2) Å, b = 13.5080(4) Å, c = 10.7647(3) Å, α = 90.00°, β = 91.337(1)°, γ = 90.00°, V = 1342.08(6) Å^3, Z = 4, μ = 0.096 mm^{-1}, T = 298 K, data/parameters = 1524/106, converging to R_1 = 0.0392, wR_2 = 0.1057 (on 1371, $I > 2\sigma(I)$ observed data); R_1 = 0.0447, wR_2 = 0.1129 (all data), residual electron density: 0.166 e/Å^3.

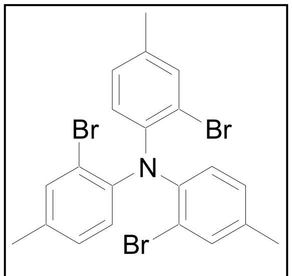


5

2-(4-Oxo-4H-benzo[d][1,3]oxazin-1-yl)-benzoic acid methyl ester. $Pd_2(dba)_3$ (0.046 g, 0.05 mmol), DPPB (0.032 g, 0.075 mmol), and methyl 2-bromobenzoate (0.168 mL, 1.2 mmol) were combined in a 50-mL Schlenk flask under argon. Dry toluene (15 mL) was added and the reaction stirred for 10 min. at room temperature. Bis(*o*-methylbenzoate)amine **1** (0.286 g, 1.0 mmol) was added followed by 0.5 M (in toluene) potassium bis(trimethylsilyl)amide (0.168 mL, 1.1 mmol) and the reaction heated to 110 °C for 48 h. The reaction was cooled to room temperature and filtered. The filtrate was concentrated by rotary evaporation and the resulting residue was purified by column chromatography using 5:2 ether:hexane as the eluent. Recrystallization from hexane gave 0.043 g (15% yield) of **5** as a clear oil that slowly formed a crystalline solid. ^{1}H NMR: ($CDCl_3$) δ 3.77 (s, 3H), 5.48 (s, 2H), 6.69 (d, *J* = 8.3 Hz, 1H), 7.06 (dt, *J* = 1.1 and 7.7 Hz, 1H), 7.25 (dd, *J* = 1.3 and 7.9 Hz, 1H), 7.37 (m, 2H), 7.55 (td, *J* = 1.7 and 7.3 Hz, 1H), 8.00 (dd, *J* = 1.7 and 7.9 Hz, 1H), 8.07 (dd, *J* = 1.7 and 7.9 Hz, 1H). Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.95. Found: C, 67.76; H, 4.51; N, 4.92. LRMS for $C_{16}H_{13}NO_4$: 283.09. Crystal data: $C_{16}H_{13}NO_4$, *M* = 284.291, Orthorhombic, *Pbca*, *a* = 8.4330(2) Å, *b* = 15.3220(7) Å, *c* = 20.9046(9) Å, α = 90.00°, β = 90.00°, γ = 90.00°,*V* = 2701.1(2)Å^3, *Z* = 8, μ = 0.101 mm^{-1}, T = 298 K, data/parameters = 3097/191, converging to R_1 = 0.0583, wR_2 = 0.1573 (on 2043, $I > 2\sigma(I)$ observed data); R_1 = 0.0960, wR_2 = 0.1862 (all data), residual electron density: 0.331 e/Å^3.

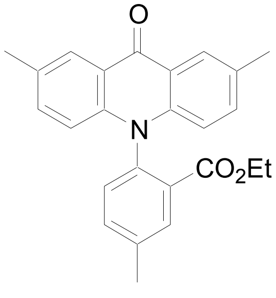
COSY NMR (300 MHz, $CDCl_3$):





6

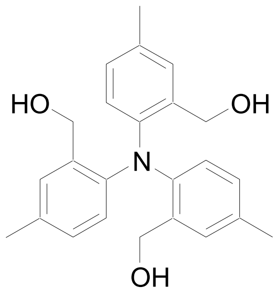
Tris-(2-bromo-4-methyl-phenyl)-amine (6). Tris(p-tolyl)amine (1.437 g, 5.0 mmol) was dissolved in 15 mL $CHCl_3$ in a 50 mL round-bottom flask. A solution of bromine (0.85 mL, 16.5 mmol) in 5 mL $CHCl_3$ was added dropwise using an addition funnel. The reaction was stirred 3 h at room temperature and then an aqueous solution of sodium thiosulfate was added. The organic layer was separated and the aqueous layer washed several times with $CHCl_3$. The combined organic layers were dried with sodium sulfate, filtered and reduced by rotary evaporation. The white solid was recrystallized with EtOH and a minimum amount of $CHCl_3$ to give 2.483 g (95% yield) of **6** after two crops. ^{1}H NMR: ($CDCl_3$) δ 2.30 (dd, *J* = 0.6 and 1.9 Hz, 9H), 6.69 (d, *J* = 8.1 Hz, 3H), 6.98 (ddd, *J* = 0.8, 2.1, and 8.3 Hz, 3H), 7.39 (dd, *J* = 0.6 and 1.9 Hz, 3H). Anal. Calcd for $C_{21}H_{18}NBr_3$: C, 48.13; H, 3.46; N, 2.67. Found: C, 47.82; H, 3.22; N, 2.61.



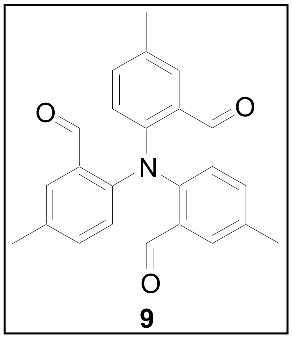
7

2-(2,7-Dimethyl-9-oxo-9H-acridin-10-yl)-5-methyl benzoic acid ethyl ester (7). Tris-(2-bromo-4-methyl-phenyl)-amine **6** (0.524 g, 1.0 mmol) was dissolved in 10 mL dry THF and cooled to -100 °C under argon. *n*-BuLi (1.32 mL, 3.3 mmol) was added dropwise and the solution stirred for 30 min. at -100 °C. Ethyl chloroformate (0.34 mL, 3.5 mmol) was added dropwise and the reaction allowed to come to room temperature over a 18 h period. A saturated aqueous solution NH_4Cl was added and the reaction mixture extracted with several portions of CH_2Cl_2. The combined organic layer was dried over sodium sulfate, filtered, and reduced by rotary evaporation. Column chromatography with 15:1 CH_2Cl_2:EtOAc as the eluent gave 0.179 g (46% yield) of **7**. ^{1}H NMR: ($CDCl_3$) δ 0.52 (t, *J* = 7.1, 3H), 2.44 (s, 6H), 2.58

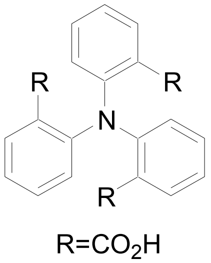
(s, 3H), 3.75 (qrt, J = 7.1 Hz, 2H), 6.57 (d, J = 8.6 Hz, 2H), 7.28 (dd, J = 2.3 and 7.7 Hz, 3H), 7.64 (dd, J = 2.3 and 8.1 Hz, 31H), 8.12 (s, 1H), 8.37 (s, 2H).


8

Tris(2-hydroxymethyl-4-methyl-phenyl)amine (8). Tris-(2-bromo-4-methyl-phenyl)-amine **6** (0.897 g, 1.7 mmol) was dissolved in 15 mL dry THF and cooled to -78 °C under argon. *n*-BuLi (2.36 mL, 6.8 mmol) was added dropwise and the solution stirred for 15 min. at room temperature. This solution was then added to paraformaldehyde (0.510 g, 17 mmol) dispersed in 10 mL THF at -78 °C. The reaction was stirred at room temperature for 18 h. A saturated aqueous solution NH_4Cl was added and the reaction mixture extracted with several portions of EtOAc. The combined organic layer was dried over sodium sulfate, filtered, and reduced by rotary evaporation. Column chromatography with 1:1 $CHCl_3$:Acetone as the eluent gave 0.510 g (79% yield) of **8**. ^{1}H NMR: ($CDCl_3$) δ 2.29 (s, 9H), 4.08 (bs, 6H), 5.22 (bs, 3H), 6.63 (d, J = 7.9, 3H), 6.93 (dd, J = 2.1, 8.1 Hz, 3H), 7.09 (d, J = 1.9 Hz, 3H). Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71. Found: C, 76.41; H, 7.26; N, 3.69.

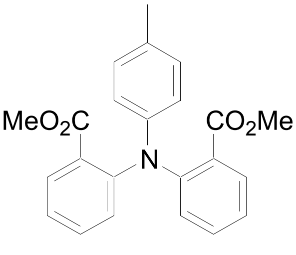

9

Tris(2-carboxaldehyde-4-methyl-phenyl)amine (9). Tris(2-hydroxymethyl-4-methyl-phenyl)amine **8** (0.450g, 1.2 mmol) and MnO_2 (2.09 g, 24 mmol) were combined with 25 mL CH_2Cl_2 in a 50 mL round-bottom flask and stirred 48 h at room temperature. The reaction was filtered and the filtrate concentrated by rotary evaporation. Column chromatography using 10:1 $CHCl_3$:Acetone as the eluent gave 0.371 g (84% yield) of **9**. ^{1}H NMR: ($CDCl_3$) δ 2.36 (s, 9H), 6.73 (d, J = 8.3, 3H), 7.25 (dd, *J* = 2.3 and 8.3, 3H), 7.63 (d, *J* = 1.9, 3H), 10.14 (s, 3H). ^{13}C NMR: ($CDCl_3$) δ 21.1, 126.3, 129.5, 132.2, 135.5, 136.2, 149.7, 190.5. Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.43; H, 5.71; N, 3.76.



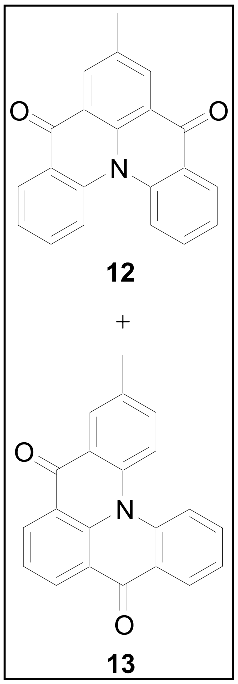
10

Tris(2-carboxylate-phenyl)amine (10). In a 250 mL round-bottom flask, equipped with a reflux condenser, *o*,*o*',*o*''-amino-trisbenzoic acid-trimethylester **2** (4.978 g, 12.0 mmol) was combined with sodium hydroxide (6.00 g, 150 mmol) in 50 mL of an ethanol/water (1:1) mixture. The reaction was heated to reflux for 3 h and then acidified with dilute hydrochloric acid to pH~2-3. The triacid precipitated as a white solid and was collected by vacuum filtration, oven dried to give 4.299 g (93% yield) of **10**. Recrystallization from a solution of ethanol/water gave small, but well-defined, colorless cubic crystals in 62% yield. Concentration of the filtrate and subsequent recrystallization gave a second crop of crystals for an overall yield of 93%. Crystal data for **1**: $C_{21}H_{15}NO_6$, M = 377.35, Cubic, P -43n (218), a = 15.8558(3) Å, V = 3986.25(13) Å^3, Z = 8, ρ = 1.415, μ = 0.105 mm^{-1}, T = 90 K, data/parameters = 1518/91, converging to R_1 = 0.0752, wR_2 = 0.2101 (on 1327, I>2σ(I) observed data); R_1 = 0.0843, wR_2 = 0.2255 (all data), residual electron density: 0.43 e/Å^3. CDCC 186794.



11

2, 2'-[(4-Methylphenyl)imino]bisbenzoicacid-dimethylester (11). *p*-Toluidine (5.36 g, 50 mmol) was coupled with methyl 2-iodobenzoate (22.4 mL, 105 mmol) in 50 mL of *n*-butylether, with K_2CO_3 (14.51 g, 105 mmol), Cu (0.75 g, 12 mmol) and CuI (0.50 g, 2.6 mmol), heated to 170 °C for 120 h. The reaction was filtered and the solvent removed by vacuum distillation. The crude product was purified by flash chromatography using 3:1 hexane/ethyl acetate as the eluent and then recrystallized from ethanol to give 12.99 g (70% yield) of **11.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, *J*=1.7, 7.7 Hz, 2H), 7.38 (dt, *J*=1.7, 8.1 Hz, 2H), 7.12 (m, 4H), 6.98 (d, *J*=8.1, 2H), 6.71 (d, *J*=8.7, 2H), 3.39 (s, 6H), 2.24 (s, 3H). Anal. Calcd. For $C_{23}H_{21}NO_4$: C=73.58, H=5.64, N=3.73; Found: C=73.29, H=5.55, N=3.69. *Crystal data*: $C_{23}H_{21}NO_4$, M = 375.42, Triclinic, $P\ \text{-}1$, a = 10.1343(2) Å, b = 10.1351(2) Å, c = 11.8738(3) Å, α = 111.00(10)°, β = 113.43(10)°, γ = 96.55(9)°, V = 996.63(4) Å^3, Z = 2, μ = 0.086 mm^{-1}, T = 298 K, data/parameters = 3470 /254, converging to R_1 = 0.0547, wR_2 = 0.1307 (on 2638, $I > 2\sigma(I)$ observed data); R_1 = 0.0798, wR_2 = 0.1685 (all data), residual electron density: 0.480 e/Å^3.

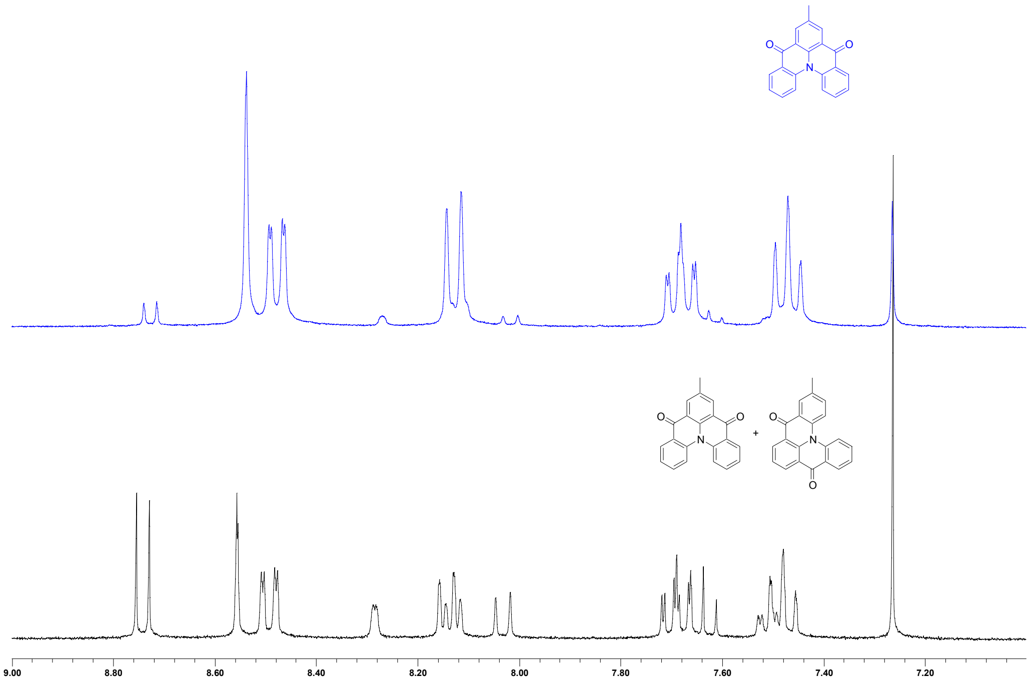


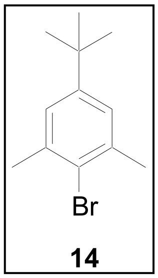
12

+

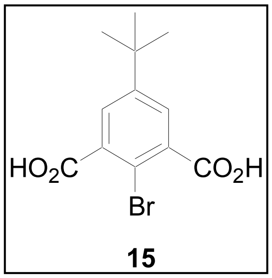
13

Synthesis of mixed symmetric (12) and unsymmetric (13) bridged triarylamines. 2, 2'-[(4-Methylphenyl)imino]bisbenzoicacid-dimethylester **11** (0.939 g, 2.5 mmol) was hydrolyzed with NaOH (0.6 g, 15 mmol) in 25 mL of refluxing ethanol/water (1:1) for 2 h. The resulting acid was precipitated with concentrated HCl and dried under vacuum. The solid was then dispersed in dichloromethane (15 mL) with a few drops of DMF and then oxalylchloride (0.44 mL, 5.1 mmol) was added dropwise. The reaction was refluxed for 1 h and $FeCl_3$ (1.62 g, 10 mmol) added. After refluxing for an additional 12 h, the reaction was filtered through celite and concentrated. Flash chromatography in using 20:1 chloroform/acetone as the eluent gave 0.417 g (53% yield) of the bridged triarylamine as a mixture of symmetric **12** and unsymmetric **13** isomers. Recrystallization from chloroform/hexane gave the symmetric isomer **12** in a more pure form. The proton NMR spectra of both the mixture and symmetric product are shown below. Also, the elemental analysis of the mixture gives: Anal. Calcd. For $C_{21}H_{13}NO_2$: C=81.01, H=4.21, N=4.50; Found: C=80.85, H=4.05, N=4.45. For the symmetric isomer **12**, *Crystal data*: $C_{21}H_{13}NO_2$, M = 311.34, Monoclinic, $P\,2_1/n$, a = 3.9442(2) Å, b = 10.3945(4) Å, c = 34.639(2) Å, α = 90.00°, β = 91.58 (10)°, γ = 90.00°,V = 1419.60(10) Å^3, Z = 4, μ = 0.094 mm^{-1}, T = 298 K, data/parameters = 2400 /97, converging to R_1 = 0.1151, wR_2 = 0.2906 (on 1349, $I > 2\sigma(I)$ observed data); R_1 = 0.1871, wR_2 = 0.3509 (all data), residual electron density: 0.599 e/Å^3.

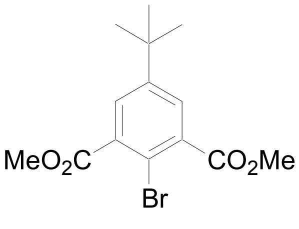



14

2-Bromo-5-*tert*-butyl-1,3-dimethylbenzene (14). In a 250 mL round bottom flask equipped with a magnetic stir bar and an addition funnel, was added 5-*t*-butyl-*m*-xylene (91.0 mL, 0.48 mol) and 1 large spatula scoop (~1g) of iron powder to 75 mL of chloroform. The solution was cooled to 0 ˚C. A solution of bromine (27.3 mL, 0.53 mol) in 22.7 mL of chloroform was added dropwise *via* the addition funnel. The reaction was stirred for 2 h at room temperature and then poured into a cold solution of dilute aqueous NaOH (~1M). The mixture was separated and the aqueous layer was washed several times with ether. The combined organic layers were dried with sodium sulfate, filtered, and concentrated to a clear oil which became a white solid upon standing. The crude solid was recrystallized from ethanol (several crops) to give 104.52 g (90% yield,) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 2H), 2.41 (s, 6H), 1.29 (s, 9H). *Crystal data*: $C_{12}H_{17}Br$, M = 241.177, Orthorhombic, *P nma*, a = 9.6439(4) Å, b = 7.3388(2) Å, c = 16.8992(8) Å, α = 90.00°, β = 90.00°, γ = 90.00°,V = 1196.04(8) Å^3, Z = 4, μ = 3.394 mm^{-1}, T = 298 K, data/parameters = 1127/77, converging to R_1 = 0.0427, wR_2 = 0.1137 (on 912, $I > 2\sigma(I)$ observed data); R_1 = 0.0550, wR_2 = 0.1247 (all data), residual electron density: 0.542 e/Å^3.

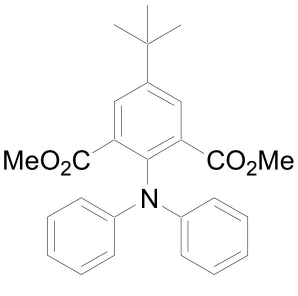

15

2-Bromo-5-*tert*-butyl-isophthalic acid (15). In a 2 L 3-necked round bottom flask equipped with a mechanical stirrer and a reflux condenser, was added 2-bromo-5-*tert*-butyl-1,3-dimethylbenzene **14** (104.5 g, 0.43 mol), dispersed in 800 mL of a 1:1 mixture of *t*-butanol and water. $KMnO_4$ (143.8 g, 0.91 mol) was added and the reaction mixture was heated to reflux for 1 h. After cooling to room temperature, more $KMnO_4$ (143.8 g, 0.91 mol) was added and the reaction mixture was refluxed for an additional 18 h. After cooling to room temperature, the reaction was filtered through celite and the filtrate was reduced by 1/3. The solution was acidified with concentrated HCl. The resulting white precipitate was collected by vacuum filtration and dissolved in aqueous $NaHCO_3$. The aqueous layer was washed with ether to remove any residual organics. The aqueous layer was then acidified with concentrated HCl, the precipitate collected and oven-dried (~80 ˚C) overnight to give 125.8 g (97% yield) of the title compound. ^1H NMR (300 MHz, CD_3OD) δ 8.61 (s, 2H), 2.19 (s, 9H). ^{13}C NMR (300 MHz, CD_3OD) δ 170.30, 152.22, 137.53, 129.81, 115.37, 35.66, 31.29.



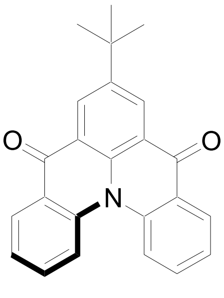
16

2-Bromo-5-*tert*-butyl-isophthalic acid dimethyl ester (16). In a 2 L round bottom flask equipped with a magnetic stir bar and a reflux condenser, was added 2-bromo-5-*tert*-butyl-isophthalic acid **15** (104.6 g, 0.35 mol), in 750 mL of methanol and 80 mL of H_2SO_4. The reaction mixture was heated to reflux for 18 h and poured into water (~500 mL). The reaction was neutralized with $NaHCO_3$ and aqueous solution was washed several times with ether. The combined organic layers were dried over sodium sulfate, filtered, and concentrated. Recrystallization from hexane gave 93.8 g (81% yield) of the title compound. ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 2H), 3.95 (s, 6H), 1.33 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.32, 150.67, 134.91, 129.42, 115.56, 52.65, 34.70, 30.84. Anal. Calcd. For $C_{14}H_{17}BrO_4$: C=51.08, H=5.21; Found: C=50.58, H=5.27.



17

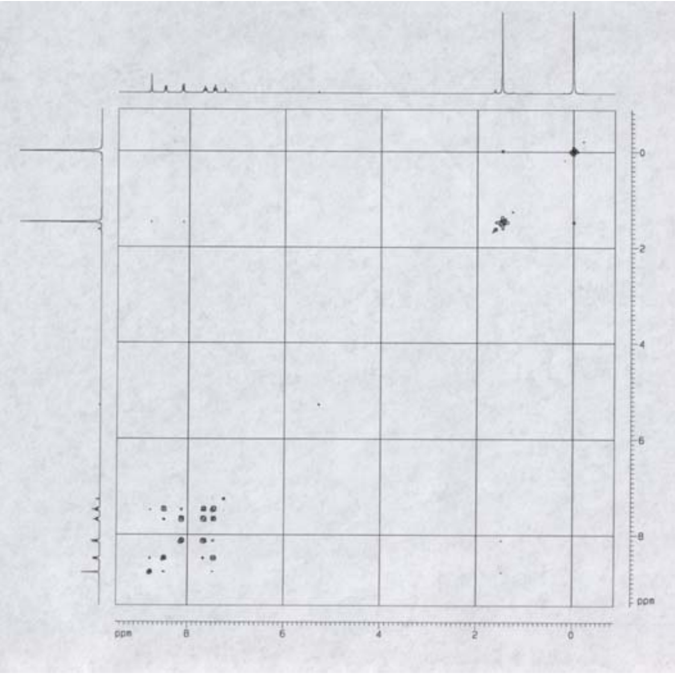
5-*tert*-Butyl-2-diphenylamino-isophthalic acid dimethyl ester (17). Diphenylamine (0.85 g, 5.0 mmol) was coupled with 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester **16** (1.81 g, 5.5 mmol), potassium carbonate (0.829 g, 6.0 mmol), and copper bronze (0.048 g, 0.75 mmol) were combined with diphenylether in a round-bottom flask equipped with a magnetic stir bar and reflux condenser. The reaction was heated to ~190 °C for 48 h under argon. The reaction was filtered, the solvent removed by vacuum distillation, and the residue purified by column chromatography using a 5:1 solution of hexane/ethyl acetate as the eluent to give 1.77 g (85% yield) of the title compound as a yellow crystalline solid. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.18 (m, 4H), 6.95 (m, 6H), 3.47 (s, 6H), 1.35 (s, 9H). ^{13}C NMR: (300 MHz, $CDCl_3$) δ 168.4, 148.9, 147.4, 142.0, 132.3, 131.1, 129.1, 122.5, 122.3, 52.5, 31.4. Anal. Calcd. For $C_{26}H_{27}NO_4$: C, 74.80; H, 6.52, N, 3.35. Found: C, 74.60; H, 6.73, N, 3.34. *Crystal data*: $C_{26}H_{27}NO_4$, M = 417.505, Monoclinic, $P\ 2_1/c$, a = 12.1636(4) Å, b = 17.4913(6) Å, c = 11.8633(3) Å, α = 90.00°, β = 110.62(13)°, γ = 90.00°,V = 2362.26(13) Å^3, Z = 4, μ = 0.079 mm^{-1}, T = 298 K, data/parameters = 4082/280, converging to R_1 = 0.0788, wR_2 = 0.1896 (on 2395, $I > 2\sigma(I)$ observed data); R_1 = 0.1397, wR_2 = 0.2252 (all data), residual electron density: 0.423 e/Å^3.

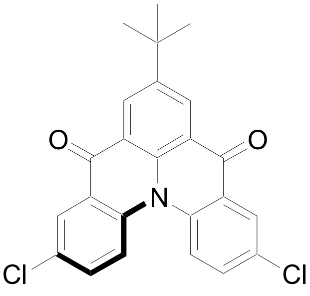


18

7-*tert*-Butyl-13b-aza-naphtho[3,2,1-de]anthracene-5,9-dione (18). 5-*tert*-Butyl-2-diphenylamino-isophthalic acid dimethyl ester **17** was hydrolyzed with sodium hydroxide (10 eq) in a solution of 1:1 ethanol/water heated to reflux for 12-72 h. Acidification with conc. Hydrochloric acid precipitated the triarylamine diacid which was collected by vacuum filtration and oven-dried (~80 °C) overnight. Yields were nearly quantitative (95-97%) and the material was used in the next step without further purification. 5-*tert*-butyl-2-diphenylamino-isophthalic acid (0.20 g, 0.5 mmol) was dispersed in dry dichloromethane in a 3-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser w/ drying tube. A few drops of N,N-dimethylformamide was added followed by oxalyl chloride (0.10 mL, 1.1 mmol). The reaction was heated to reflux for 0.5 h. Tin(IV) chloride (0.13 mL, 1.1 mmol) was added and the reaction refluxed for an additional 2 h. The reaction mixture was added dropwise to an aqueous solution of sodium hydroxide (~1M) and extracted with dichloromethane. The organic layer was collected and dried over sodium sulfate, filtered, and concentrated. The crude product was then purified by flash chromatography using 3:1 hexane/ethyl acetate as the eluent to give 0.14 g (80% yield) of **18.** ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.48 (dd, *J*=1.7, 7.9 Hz, 2H), 8.12 (d, *J*=8.6 Hz, 2H), 7.67 (dt, *J*=1.7, 8.6 Hz, 2H), 7.46 (dt, *J*=0.9, 7.9 Hz, 2H), 1.48 (s, 9H). ^{13}C NMR: (300 MHz, $CDCl_3$) δ 178.75, 147.09, 139.62, 137.43, 132.53, 129.84, 127.80, 126.35, 124.95, 123.16, 120.03, 35.00, 31.30. HRMS Calcd for $C_{24}H_{19}NO_2$: 353.1416 Found: 353.1411. MP=247-249 °C. *Crystal data*: $C_{24}H_{19}NO_2$, M = 353.1416, Orthorhombic, *P bcn*, a = 12.2443(13) Å, b = 12.454(2) Å, c = 11.9541(13) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 1822.9(4) Å^3, Z = 4, μ = 0.080 mm^{-1}, T = 298 K, data/parameters = 1571/138, converging to R_1 = 0.1638, wR_2 = 0.3901 (on 1043, $I > 2\sigma(I)$ observed data); R_1 = 0.2089, wR_2 = 0.4183 (all data), residual electron density: 0.493 e/Å^3.

COSY NMR (300 MHz, $CDCl_3$):

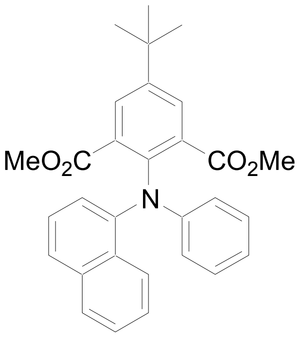




19

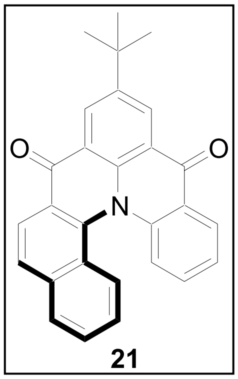
19. 5-*tert*-butyl-2-diphenylamino-isophthalic acid (0.667 g, 1.7 mmol) was dispersed in thionyl chloride in a 3-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser w/ drying tube. A few drops of N,N-dimethylformamide was added and the reaction was heated to reflux for 3 h. Thionyl chloride was removed by vacuum distillation and replaced with dry dichloromethane. Iron(III) chloride (1.11 g, 6.8 mmol) was added and the reaction refluxed for an additional 18 h. The reaction mixture filtered through celite and partitioned between dichloromethane and water. The organic layer was collected and dried over sodium sulfate, filtered, and concentrated. The crude product was then purified by flash chromatography using chloroform as the eluent to give 0.18 g (25% yield) of **19.** *Crystal data*: $C_{24}H_{17}Cl_2NO_2$, M = 422.311, Monoclinic, $C\ 2/c$, a = 19.7594(5) Å, b = 16.0151(5) Å, c = 14.5700(3) Å, α = 90.00°, β = 118.715(2)°, γ

= 90.00°,V = 4043.6(2) Å^3, Z = 8, μ = 0.342 mm^{-1}, T = 298 K, data/parameters = 3526/262, converging to R_1 = 0.0655, wR_2 = 0.1716 (on 1043, $I > 2\sigma(I)$ observed data); R_1 = 0.0968, wR_2 = 0.1940 (all data), residual electron density: 1.126 e/Å^3.



20

5-*tert*-Butyl-2-(naphthalen-1-yl-phenyl-amino)-isophthalic acid dimethyl ester (20). N-phenyl-1-naphthylamine (1.10 g, 5.0 mmol) was coupled with 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester **16** (1.81 g, 5.5 mmol), potassium carbonate (0.829 g, 6.0 mmol), and copper bronze (0.048 g, 0.75 mmol) were combined with diphenylether in a round-bottom flask equipped with a magnetic stir bar and reflux condenser. The reaction was heated to ~190 °C for 48 h under argon. The reaction was filtered, the solvent removed by vacuum distillation, and the residue purified by column chromatography using a 3:1 solution of dichloromethane/hexane as the eluent to give 1.48 g (63% yield) of the title compound. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.83 (d, J=8.2 Hz, 1H), 7.72 (d, J=8.3 Hz, 1H), 7.63 (s, 2H), 7.63 (d, J=8.1 Hz, 1H), 7.38 (t, J=8.1 Hz, 2H), 7.25 (dt, J=7.4, 1.0 Hz, 2H), 7.12 (t, J=8.3 Hz, 2H), 6.87 (dt, J=7.4, 1.0 Hz, 1H), 6.74 (br d, J=8.2 Hz, 2H), 3.14 (br s, 6H), 1.35 (s, 9H). ^{13}C NMR: (300 MHz, $CDCl_3$) δ 168.3, 148.6, 147.8, 142.7, 142.7, 134.8, 131.7, 129.8, 128.6, 128.2, 126.1, 125.9, 125.5, 125.3, 125.0, 124.9, 121.21, 120.64, 52.0, 34.6, 31.08. HRMS Calcd for $C_{30}H_{29}NO_4$: 467.2097 Found: 467.2061. MP=220-222 °C.

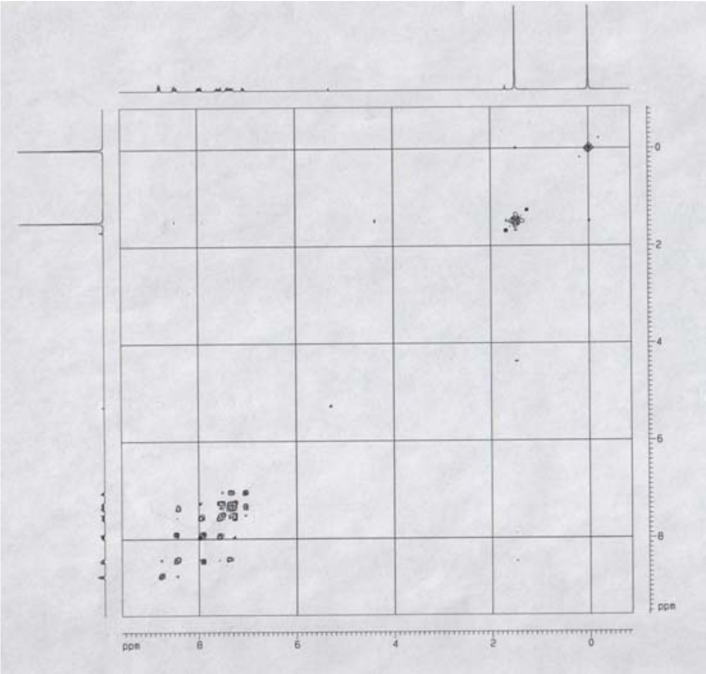


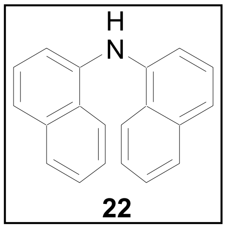
21

(21). 5-*tert*-Butyl-2-(naphthalen-1-yl-phenyl-amino)-isophthalic acid dimethyl ester **20** was hydrolyzed with sodium hydroxide (10 eq) in a solution of 1:1 ethanol/water heated to reflux for 12-72 h. Acidification with conc. Hydrochloric acid precipitated the triarylamine diacid which was collected by vacuum filtration and oven-dried (~80 °C) overnight. Yields were nearly quantitative (95-97%) and the material was used in the next step without further purification. 5-*tert*-butyl-2-(naphthalen-1-yl-phenyl-amino)isophthalic acid (1.34 g, 3.26 mmol) was dispersed in dry dichloromethane in a 3-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser w/ drying tube. A few drops of N,N-dimethylformamide was added followed by oxalyl chloride (0.63 mL, 7.2 mmol). The reaction was heated to reflux for 0.5 h. Tin(IV) chloride (0.83 mL, 7.2 mmol) was added and the reaction refluxed for an additional 2 h. The reaction mixture was added dropwise to an aqueous solution of sodium hydroxide (~1M) and extracted with dichloromethane. The organic layer was collected and dried over sodium sulfate, filtered, and concentrated. The crude product was then purified by flash chromatography using 5:1 dichlormethane/hexane as the eluent to give 0.95 g (78% yield) of **21.** ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.77 (dd, *J*=2.4, 9.2 Hz 2H), 8.48 (d, *J*=8.7 Hz, 1H), 8.43 (dd, *J*=2.1, 7.5 Hz, 1H), 7.98 (d, *J*=8.1 Hz, 1H), 7.93 (d, *J*=8.5 Hz, 1H), 7.59 (dt, *J*=1.1, 8.1 Hz, 1H), 7.53 (d, *J*=8.7 Hz, 1H), 7.37 (m, 3H), 7.07 (d, *J*=9.2 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR: (300 MHz, $CDCl_3$) δ 179.76, 178.89, 147.56, 142.08, 138.76, 137.70, 136.35, 131.84, 129.53, 129.06, 128.95, 128.54, 127.49, 127.11, 126.60, 125.60, 125.56, 124.79, 124.73, 124.71, 124.04, 123.66, 122.16, 121.30, 35.10, 31.34. HRMS Calcd for $C_{28}H_{21}NO_2$: 403.1572 Found: 403.1597. MP=319-321 °C. *Crystal data*: $C_{28}H_{21}NO_2$, *M* = 403.481, monoclinic, *P2₁/c* (no. 14), *a* = 8.8628(2) Å, *b* = 11.4131(3) Å, *c* = 20.4548(7) Å, α = 90.00°, β = 93.29 (1)°, γ = 90.00°,

V=2065.63(10) Å^3, Z = 4, μ = 0.081 mm^{-1}, T = 298 K, data/parameters = 3608/280, converging to R_1 = 0.0680, wR_2 = 0.1927 (on 2484, $I > 2\sigma(I)$ observed data); R_1 = 0.1004, wR_2 = 0.2092 (all data), residual electron density: 0.479 e/Å^3.

COSY NMR (300 MHz, $CDCl_3$):

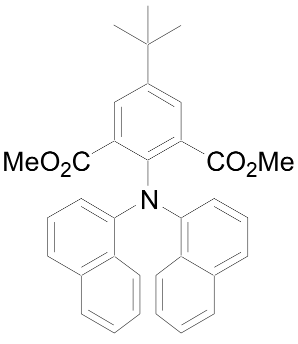




22

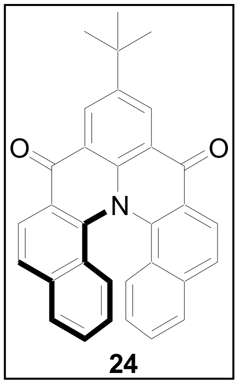
Dinaphthylamine (22). A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with 1-aminonaphthalene (8.591 g, 60.0 mmol), $Pd_2(dba)_3$ (1.094 g, 1.2 mmol), 1,1' bis (diphenylphosphino) ferrocene (0.998 g, 1.8 mmol), and sodium-*t*-butoxide (7.208 g, 75.0 mmol). Air was removed and replaced by argon. Dry toluene (40 mL) was added through a septum followed by the addition of 1-bromonaphthalene (8.34 mL, 60.0 mmol). The septum was replaced with a glass stopper and the reaction stirred for 48 h at 110 °C. The resulting mixture was cooled to room temperature and the solids filtered out with CH_2Cl_2 as a wash solvent. Solvents were removed by rotary evaporation. The residue was purified by flash chromatography with 2:1

hexane/dichloromethane as the eluent to give the product as a yellow solid. Recrystallization from dichloromethane layered with hexane gave the product as yellow crystals (13.243 g, 82%). The product oxidizes to a red solid when left in air for over 1 h. However, the product can be stored under argon at -40 °C for up to several months. ^{1}H NMR: ($CDCl_3$) δ 8.08 (d, *J*=8.0 Hz, 2H), 7.89 (d, *J*=7.5 Hz, 2H), 7.50 (m, 6H), 7.34 (t, *J*=7.9 Hz, 2H), 7.02 (d, *J*=7.4 Hz, 2H), 6.34 (br s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 140.24, 134.60, 128.58, 126.87, 126.16, 126.07, 125.62, 122.34, 121.76, 115.38. HRMS Calcd For $C_{20}H_{15}N$: 269.1204 Found: 269.1202. *Crystal data*: $C_{20}H_{15}N$, M = 269.347, Monoclinic, $P\ 2_1/c$, a = 10.4907(7) Å, b = 10.9269(7) Å, c = 14.5995(12) Å, α = 90.00°, β = 120(18)°, γ = 90.00°,V = 1431.8(2) Å^3, Z = 4, μ = 0.072 mm^{-1}, T = 298 K, data/parameters = 2494/192, converging to R_1 = 0.0640, wR_2 = 0.1743 (on 1660, $I > 2\sigma(I)$ observed data); R_1 = 0.0985, wR_2 = 0.2057 (all data), residual electron density: 0.436 e/Å^3.



23

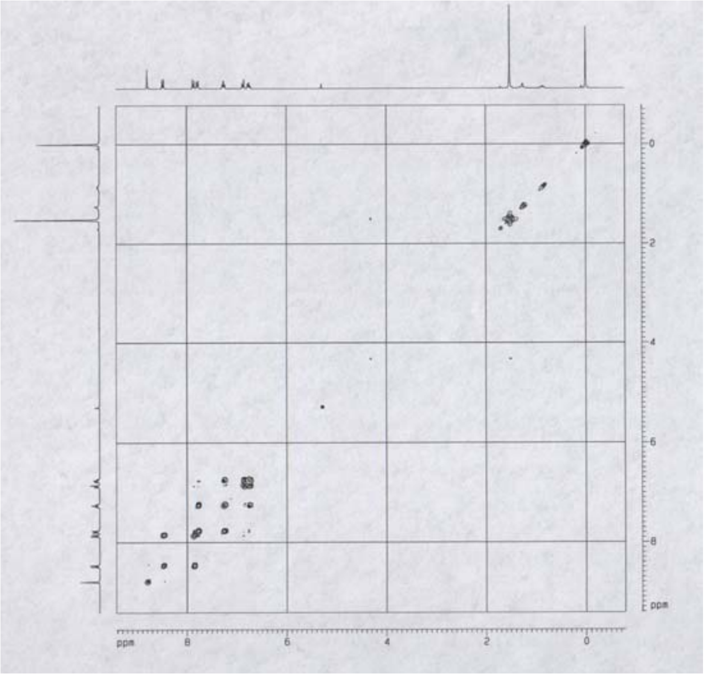
5-*tert*-Butyl-2-(di-naphthalen-1-yl-amino)-isophthalic acid dimethyl ester (23). Dinaphthylamine (1.34 g, 5.0 mmol) was coupled with 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester **16** (6.0 g, 17.93 mmol) in 25 mL of *n*-butylether, with K_2CO_3 (1.382 g, 10 mmol) and CuI (1.143 g, 6.0 mmol), heated to 150 °C for 120 h. The reaction was filtered and the solvent removed by vacuum distillation. The crude product was purified by flash chromatography using 3:1 dichloromethane/hexane as the eluent to give 0.61 g (24% yield) of the title compound. NMR spectra were difficult to interpret precisely due to large peak broadening, however, further conformation of structure can be made by HRMS and X-ray crystallography. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.10 (br s), 7.80 (d, *J*=8.1 Hz), 7.59 (br s), 7.36 (br s), 6.75 (br s), {Aromatic region 6.6-8.4, 16H}, 2.6-3.3 (br d, 6H), 1.30 (s, 9H). ^{13}C NMR: (300 MHz, $CDCl_3$) δ 31.0, 34.5, 51.7, 125.5, 125.6, 128.1, 128.2, 135.0, 143.6, 144.6, 146.5, 168.6. HRMS Calcd for $C_{34}H_{31}NO_4$: 517.2253 Found: 517.2252. MP=194-196 °C. *Crystal data*: $C_{34}H_{31}NO_4$, M = 517.652, Triclinic, $P\ \bar{1}$ *-1*, a = 10.9431(3) Å, b = 11.7705(3) Å, c = 12.3238(3) Å, α = 99.21(14)°, β = 92.74(13)°, γ = 115.08(11)°, V = 1407.17(6) Å^3, Z = 2, μ = 0.080 mm^{-1}, T = 298 K, data/parameters = 4892/352, converging to R_1 = 0.0498, wR_2 = 0.1119 (on 3474, $I > 2\sigma(I)$ observed data); R_1 = 0.0788, wR_2 = 0.1282 (all data), residual electron density: 0.184 e/Å^3.


24

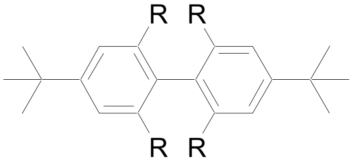
(24). 5-*tert*-Butyl-2-(di-naphthalen-1-yl-amino)-isophthalic acid dimethyl ester **23** was hydrolyzed with sodium hydroxide (10 eq) in a solution of 1:1 ethanol/water heated to reflux for 12-72 h. Acidification with conc. Hydrochloric acid precipitated the triarylamine diacid which was collected by vacuum filtration and oven-dried (~80 °C) overnight. Yields were nearly quantitative (95-97%) and the material was used in the next step without further purification. 5-*tert*-butyl-2-(di-naphthalen-1-yl-amino)isophthalic acid (0.98 g, 2.0 mmol) was dispersed in dry dichloromethane in a 3-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser w/ drying tube. A few drops of N,N-dimethylformamide was added followed by oxalyl chloride (0.44 mL, 5.0 mmol). The reaction was heated to reflux for 0.5 h. Tin (IV) chloride (0.58 mL, 5.0 mmol) was added and the reaction refluxed for an additional 3 h. The reaction mixture was added dropwise to an aqueous solution of sodium hydroxide (~1M) and extracted with dichloromethane. The organic layer was collected and dried over sodium sulfate, filtered, and concentrated. The crude product was then purified by flash chromatography using dichloromethane as the eluent to give

0.55 g (60% yield) of **3**. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.80 (s, 2H), 8.48 (d, *J*=8.6 Hz, 2H), 7.86 (d, *J*=8.6 Hz, 2H), 7.78 (d, *J*=8.1 Hz, 2H), 7.26 (t, *J*=8.1 Hz, 2H), 6.87 (d, *J*=8.6 Hz, 2H), 6.76 (t, *J*=8.6, 2H), 1.52 (s, 9H). ^{13}C NMR: (300 MHz, $CDCl_3$) δ 179.51, 147.95, 141.01, 138.91, 135.86, 128.83, 128.50, 128.10, 126.26, 125.71, 125.48, 124.83, 124.34, 124.05, 122.00, 35.18, 31.39. HRMS Calcd for $C_{32}H_{23}NO_2$: 453.1729 Found: 453.1718. *Crystal data*: $C_{32}H_{23}NO_2$, M = 453.541, monoclinic, $C\ 2/c$, a = 17.986(2) Å, b = 13.832(2)Å, c = 11.967(2) Å, α = 90.00°, β = 128.57(6)°, γ = 90.00°,V = 2327.7(5) Å^3, Z = 4, μ = 0.080 mm^{-1}, T = 298 K, data/parameters = 1156/165, converging to R_1 = 0.1242, wR_2 = 0.3322 (on 696, $I > 2\sigma(I)$ observed data); R_1 = 0.1827, wR_2 = 0.3715 (all data), residual electron density: 0.580 e/Å^3.

COSY NMR (300 MHz, $CDCl_3$):



Also isolated from this reaction mixture were small quantities of :

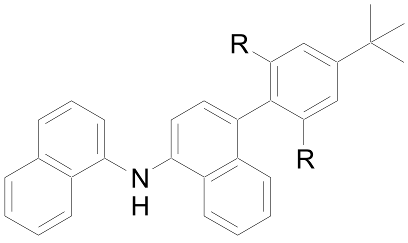


25

R=CO_2Me

Crystal data: $C_{28}H_{34}O_8$, *M* = 498.572, Orthorhombic, *P cab*, *a* = 13.72120(10) Å, *b* = 15.75360(10) Å, *c* = 25.1799(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°,*V* = 5442.84(8) Å^3, *Z* = 8, μ = 0.089 mm^{-1}, T = 298 K, data/parameters = 4761/325, converging to R_1 = 0.0895, wR_2 = 0.2527 (on 696, $I > 2\sigma(I)$ observed data); R_1 = 0.1105, wR_2 = 0.2741 (all data), residual electron density: 0.749 e/Å^3.

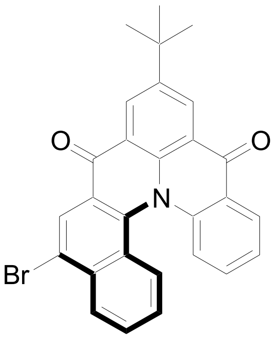
And:



26

R=CO_2Me

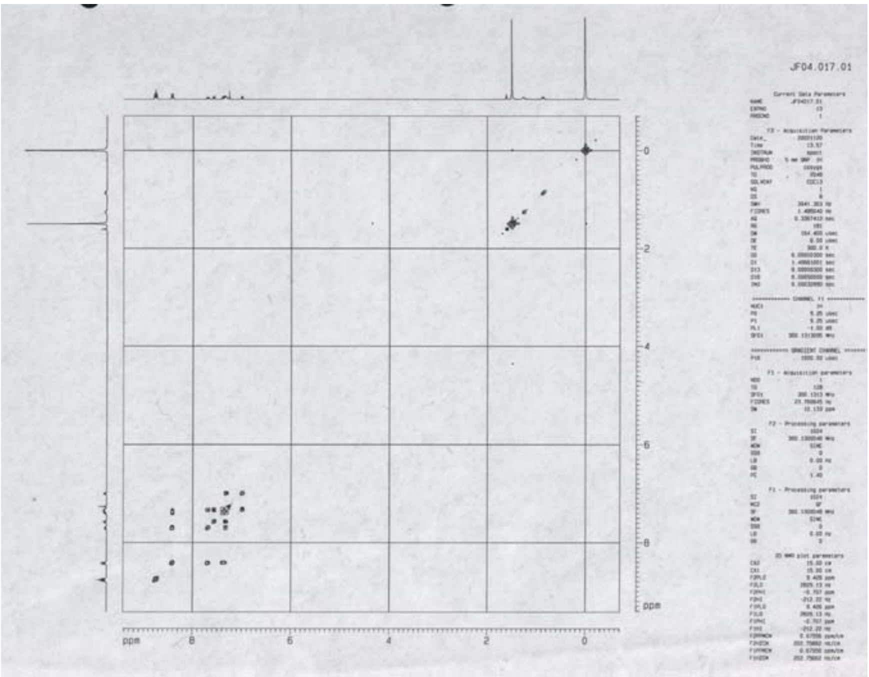
^{1}H NMR: (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 3.38 (s, 6H), 6.39 (s, 1H), 7.01 (dd, *J* = 0.9 and 7.3 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 2H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.39-7.55 (m, 6H), 7.89 (d, *J* = 7.7 Hz, 1H), 8.04 (s, 2H), 8.11 (t, *J* = 8.7 Hz, 2H). *Crystal data*: $C_{34}H_{31}NO_4$, *M* = 517.625, Monoclinic, *P 21/a*, *a* = 9.0608(2) Å, *b* = 20.8548(7) Å, *c* = 15.2714(4) Å, α = 90.00°, β = 106.951(2)°, γ = 90.00°,*V* = 2760.33(13) Å^3, *Z* = 4, μ = 0.081 mm^{-1}, T = 298 K, data/parameters = 4850/352, converging to R_1 = 0.0992, wR_2 = 0.2380 (on 696, $I > 2\sigma(I)$ observed data); R_1 = 0.1919, wR_2 = 0.2902 (all data), residual electron density: 0.470 e/Å^3.

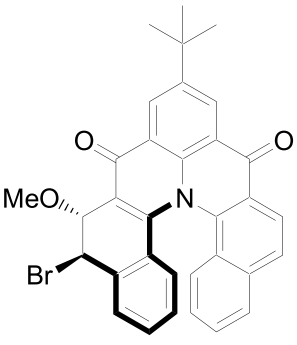


27

27. A solution of bromine (0.17 mL, 3.3 mmol) in 10 mL $CHCl_3$ was added dropwise to **21** (0.563 g, 1.5 mmol) in 20 mL $CHCl_3$ at room temperature. The reaction was stirred for 2.5 h and then partitioned between $CHCl_3$ and 1M aqueous NaOH. The organic layers were collected, dried over sodium sulfate, and reduced by rotary evaporation. Column chromatography using 1:1 Et_2O:Hexane as the eluent gave 0.196 g (27% yield) of **27** as a clear oil. Et_2O was immediately added and crystals formed after approx. 5 min. MP = 256-258 °C. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 1.50 (s, 9H), 7.00 (d, J = 8.3 Hz, 1H), 7.30-7.43 (m, 3H), 7.58 (d, J = 8.3 Hz, 1H), 7.71 (t, J = 8.5 Hz, 1H), 8.43 (d, J = 7.7 Hz, 2H), 8.77 (t, J = 8.1, 3H). ^{13}C NMR: (300 MHz, $CDCl_3$) δ 31.3, 35.1, 120.8, 121.2, 123.5, 124.1, 125.0, 125.7, 125.8, 126.0, 126.3, 127.2, 127.9, 128.4, 129.1, 129.8, 129.9, 131.9, 134.4, 137.3, 138.7, 142.1, 147.9, 177.6, 179.6. HRMS Calcd for $C_{28}H_{20}NO_2Br$: 481.0677 Found: 481.0668. *Crystal data*: $C_{28}H_{20}BrNO_2$, M = 481.0677, Monoclinic, *P 21/c*, a = 10.2619(3) Å, b = 20.1358(6) Å, c = 11.5797(3) Å, α = 90.00°, β = 111.615(2)°, γ = 90.00°, V = 2224.47(11) Å^3, Z = 4, μ = 1.873 mm^{-1}, T = 298 K, data/parameters = 3875/291, converging to R_1 = 0.0519, wR_2 = 0.1028 (on 1043, $I > 2\sigma(I)$ observed data); R_1 = 0.0907, wR_2 = 0.1188 (all data), residual electron density: 0.285 e/Å^3.

COSY NMR (300 MHz, $CDCl_3$):

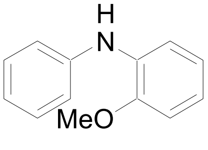




28

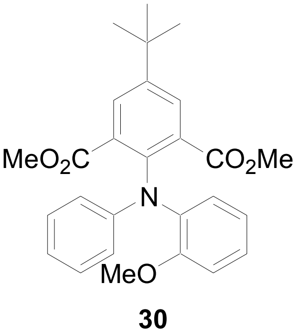
28. BTMA·Br_3 (0.214 g, 0.55 mmol), $CaCO_3$ (0.060 g, 0.6 mmol), and **24** (0.227 g, 5 mmol) were combined with 15 mL CH_2Cl_2, 6 mL MeOH, and 5 mL of $CHCl_3$. The reaction was stirred at room temperature for 18 h. The solvent was removed by rotary evaporation and the residue purified by column chromatography using 3:1 Hexane:EtOAc as the eluent. 0.213 (75%) of **28** was obtained as orange crystals after recrystallization from CH_2Cl_2 layered with hexane. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 1.51 (s, 9H), 3.46 (s, 6H), 5.50 (d, *J* = 2.1 Hz, 1H), 5.59 (d, *J* = 2.1 Hz, 1H), 6.36 (d, *J* = 7.9 Hz, 1H), 6.60 (td, *J* = 1.3 and 7.5 Hz, 1H), 7.05 (td, *J* = 1.1 and 7.5 Hz, 1H), 7.15 (dt, *J* = 1.3 and 7.2 Hz, 1H), 7.31-7.38 (m, 2H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 8.19 (dd, *J* = 0.8 and 8.7 Hz, 1H), 8.42 (d, *J* = 8.7 Hz, 1H), 8.76 (d, *J* = 2.4 Hz, 1H), 8.79 (d, *J* = 2.6 Hz, 1H). *Crystal data*: $C_{33}H_{26}BrNO_3{\cdot}O_2$, *M* = 596.477, Triclinic, *P -1*, *a* = 11.2541(3) Å, *b* = 11.6884(3) Å, *c* =

12.0775(4) Å, α = 72.6152(10)°, β = 72.8902(9)°, γ = 75.1012(12)°, V = 1423.88(7) Å^3, Z = 2, μ = 1.486 mm^{-1}, T = 298 K, data/parameters = 4969/351, converging to R_1 = 0.0643, wR_2 = 0.1724 (on 1043, $I > 2\sigma(I)$ observed data); R_1 = 0.0914, wR_2 = 0.1961 (all data), residual electron density: 0.722 e/Å^3.



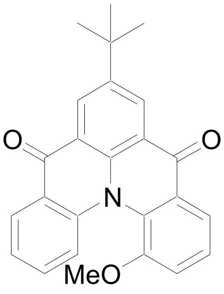
29

(2-Methoxy-phenyl)-phenyl-amine (29). *o*-anisidine (2.82 mL, 25 mmol), iodobenzene (2.80 mL, 25 mmol), $Pd_2(dba)_3$ (0.572 g, 0.625 mmol), bis(diphenylphosphino)ferrocene (0.520 g, 0.938 mmol), and sodium *t*-butoxide (3.604 g, 37.5 mmol) were combined in a 100 mL Schlenk flask under argon. Dry toluene (20 mL) was added and the reaction vessel sealed. The reaction was heated to 110 °C for 12 h. A saturated aqueous solution of NH_4Cl (5 mL) was added and the organic layer removed using a separatory funnel. The aqueous layer was washed with three, 5 mL portions of toluene. The combined organic layers were dried over sodium sulfate, filtered, and the toluene removed by rotary evaporation. The residue was then purified by flash chromatography using 4:1 hexane/ethyl acetate as the eluent. The title product was obtained in quantitative yield as a light orange liquid that was used without further purification. The proton NMR matched that reported in literature. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 3.89 (s, 9H), 6.15 (s, 1H), 6.84-6.89 (m, 3H), 6.94 (t, J = 7.4 Hz, 1H), 7.13-7.16 (m, 2H), 7.28-7.32 (m, 2H).



30

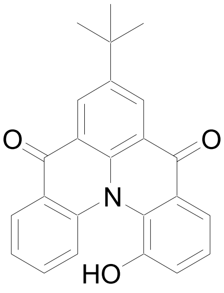
30. (2-Methoxy-phenyl)-phenyl-amine (2.66 g, 13.3 mmol), 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester (4.39 g, 13.3 mmol), copper (0.085 g, 1.33 mmol), copper(I)iodide (0.168 g, 0.88 mmol), and potassium carbonate (2.76 g, 20.0 mmol) were combined in a 50 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser. 25 mL of di-*n*-butylether was added and the reaction heated to 150 °C under argon for 96 h. The solvent was removed under dynamic vacuum and the residue was filtered using dichloromethane as a wash solvent. The filtrate was reduced by rotary evaporation and the residue was then purified by flash chromatography using 4:1 hexane/ethyl acetate as the eluent. The product was then recrystallized from ethanol to give 4.16 g of **30** (70% yield) as a yellow solid. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 1.34 (s, 9H), 3.42 (s, 6H), 3.55 (s, 3H), 6.77 (d, J = 8.5 Hz, 2H), 6.82 (m, 1H), 6.86 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 7.13 (t, J = 8.1 Hz, 2H), 7.67 (s, 2H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 31.1, 34.6, 51.9, 55.5, 112.7, 120.2, 120.8, 121.0, 124.7, 127.0, 128.1, 130.1, 131.3, 135.0, 142.2, 147.5, 147.8, 153.4, 166.4. HRMS Calcd For $C_{27}H_{29}NO_5$: 447.2046 Found: 447.2049.



31

31. Compound **30** (5.30 g, 12 mmol) and NaOH (4.74 g, 120 mmol) was heated to reflux in 40 mL of 1:1 ethanol/water for 24 h. Ethanol was removed by rotary evaporation, diluted with 10 mL of water, and acidified with concentrated hydrochloric acid. The resulting precipitate was collected by vacuum filtration and washed with copious portions of distilled water. The solid was dried in a 80 °C oven for 12 h to give 5.02 g of the diacid of **30** (quantitative yield). Recrystallization from ethanol/water mixture gave crystals suitable for single crystal X-ray diffraction. Crystal data: $C_{25}H_{25}NO_5$, M = 419.477, Monoclinic, $P\,2_1/c$, a = 8.7377(2) Å, b = 12.1684(2) Å, c = 21.1760(5) Å, a = 90.00°, b = 104.557°, g = 90.00°, V = 2179.23(8) Å^3, Z = 4, μ = 0.089 mm^{-1}, T = 298 K, data/parameters = 3833/280, converging to R_1 = 0.0563, wR_2 = 0.1431 (on 2785, $I > 2\sigma(I)$ observed data); R_1 = 0.0814, wR_2 = 0.1608 (all data), residual electron density: 0.512 e/Å^3.

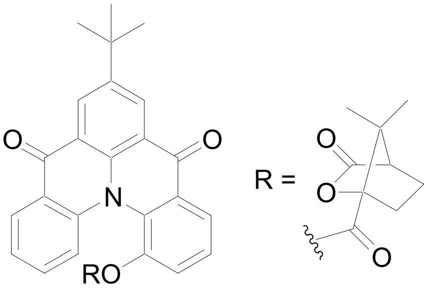
The diacid (1.26 g, 3.0 mmol) was dispersed in 25 mL of dry dichloromethane in a 50 mL, 3-neck round bottom flask equipped with a magnetic stir bar and reflux condenser. Under an argon atmosphere, a few drops of DMF was added, followed by thionyl chloride (1.31 mL, 18 mmol). The reaction was heated to reflux for 2 h, cooled slightly, and $SnCl_4$ (2.07 mL, 18 mmol) added. The reaction was heated to reflux for an additional 18 h, cooled to room temperature, and added dropwise to 50 mL of a 1M aqueous solution of NaOH. The aqueous layer was washed with several portions of dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The residue was then purified by flash chromatography using 1:1 hexane/ethyl acetate as the eluent, to give 0.921 g of **31** (80% yield). ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 1.47 (s, 9H), 3.74 (s, 3H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.29 (dd, *J* = 8.1 and 1.2 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.53 (m, 2H), 8.37 (dd, *J* = 7.9 and 1.6 Hz, 1H), 8.68 (d, *J* = 2.5 Hz, 1H), 8.76 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 31.3, 35.0, 55.5, 116.0, 119.3, 120.8, 123.1, 123.8, 123.9, 124.8, 125.8, 126.2, 129.0, 129.1, 129.8, 131.0, 138.7, 140.5, 146.9, 150.7, 179.4, 179.7. HRMS Calcd For $C_{25}H_{21}NO_3$: 383.1521 Found: 383.1572.



32

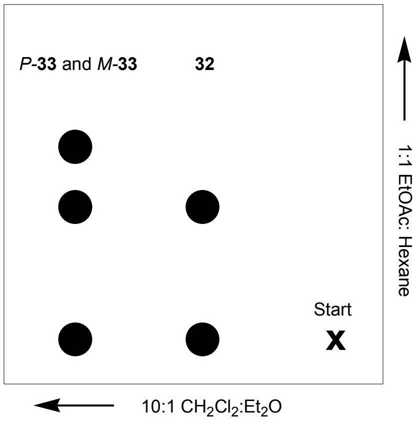
32. Compound **31** (0.720 g, 1.9 mmol) was heated to reflux in 60 mL of 1:2 mixture of acetic acid/hydrobromic acid for 72 h. The reaction was poured into 100 mL of water and filtered. The filtrate was extracted with several portions of dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and the solvent removed by rotary evaporation. The solvent was removed by rotary evaporation and the residue was then purified by flash chromatography using 10:1 dichloromethane/ether as the eluent, to give 0.451 g of **32** (60% yield). ^{1}H NMR: (DMSO-

d_6, 300 MHz) δ 1.42 (s, 9H), 7.41 (m, 4H), 7.69 (t, *J* = 7.7, 1H), 7.81 (dd, *J* = 7.7 and 1.4 Hz, 1H), 8.17 (dd, *J* = 7.9 and 1.2 Hz, 1H), 8.52 (d, *J* = 2.4 Hz, 1H), 8.58 (d, *J* = 2.4 Hz, 1H), 10.77 (s, 1H). ^{13}C NMR: (DMSO-d_6, 300 MHz) δ 30.8, 34.4, 116.9, 121.0, 121.8, 122.5, 123.0, 123.7, 123.8, 124.9, 126.1, 126.8, 128.1, 128.2, 128.4, 131.5, 138.0, 139.3, 145.8, 148.7, 178.2, 178.3. HRMS Calcd For $C_{24}H_{19}NO_3$: 369.1365 Found: 369.1363.



33

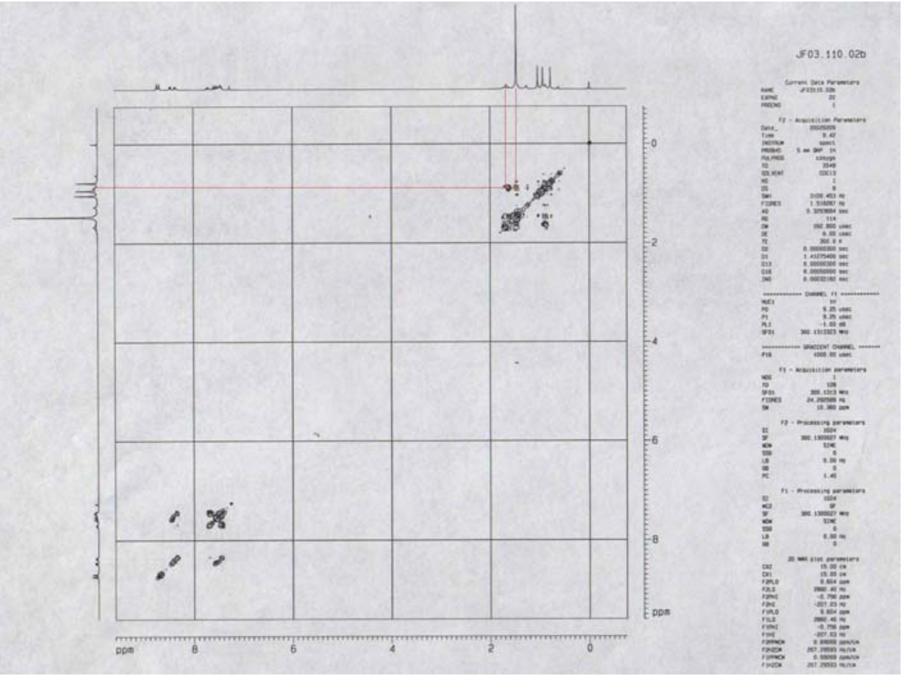
33. Compound **32** (0.300 g, 0.81 mmol) and DMAP (0.149 g, 1.2 mmol) were dissolved in 15 mL of dry dichloromethane. (1*S*)-camphanic chloride (0.352 g, 1.6 mmol) was added and the reaction heated to reflux for 12 h. The residue was then purified by flash chromatography using 10:1 dichloromethane/ether as the eluent to remove the racemic product mixture from any remaining **32**. A second column using 1:1 hexane/ethyl acetate as the eluent gave 0.194 g of *M*-**33** and 0.185 g of *P*-**33** (combined 85% yield of **33**). The 2-D TLC plate illustrated below shows that both columns are necessary to obtain the pure products.



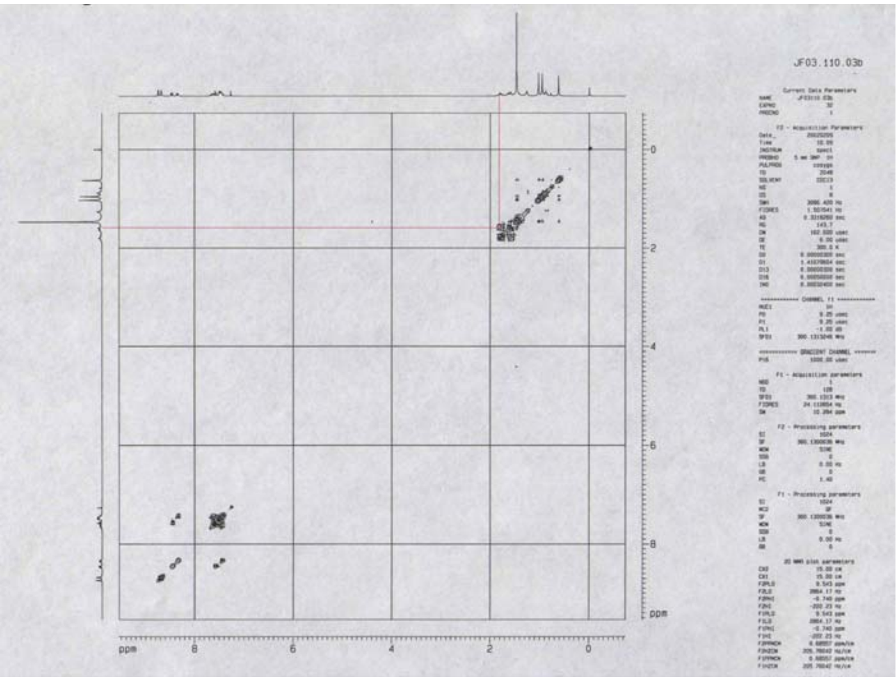
For *M*-**33**: ^{1}H NMR: (CDCl$_3$, 300 MHz) δ 0.79 (s, 3H), 0.89 (m, 1H), 0.94 (s, 3H), 1.04 (s, 3H), 1.47 (bs, 10H), 1.67 (m, 2H), 7.43-7.61 (m, 4H), 7.71 (t, *J* = 7.2 Hz, 1H), 8.37 (dd, *J* = 7.7 and 1.1 Hz, 1H), 8.47 (dd, *J* = 7.5 and 1.7 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.75 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR: (CDCl$_3$, 300 MHz) δ 9.5, 16.4, 16.6, 28.6, 29.7, 31.3, 35.0, 54.6, 54.8, 90.0, 120.2, 123.1, 123.8, 125.1, 125.2, 125.7, 126.1, 126.8, 127.7, 129.3, 129.5, 130.0, 131.9, 133.1, 138.2, 139.1, 140.2, 147.7, 164.3, 177.5, 178.6, 179.3. HRMS Calcd For $C_{34}H_{31}NO_6$: 549.2151 Found: 549.2156.

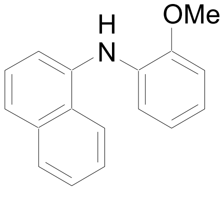
For *P*-**33**: ^{1}H NMR: (CDCl$_3$, 300 MHz) δ 0.63 (s, 3H), 0.96 (s, 3H), 1.03 (s, 3H), 1.47 (s, 9H), 1.60 (m, 2H), 1.81 (m, 2H), 7.42-7.52 (m, 3H), 7.58 (t, *J* = 7.7, 1H), 7.65 (td, *J* = 7.2 and 1.7 Hz), 8.35 (dd, *J* = 7.9 and 1.5 Hz, 1H), 8.47 (dd, *J* = 7.7 and 1.7 Hz, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.74 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR: (CDCl$_3$, 300 MHz) δ 9.5, 16.4, 16.7, 28.7, 30.4, 31.3, 35.1, 54.3, 54.5, 89.9, 119.7, 123.1, 123.9, 124.9, 125.4, 125.6, 126.1, 127.1, 127.8, 129.3, 129.5, 130.2, 132.0, 132.6, 138.4, 139.8, 140.6, 147.7, 164.9, 176.8, 178.6, 179.1. HRMS Calcd For $C_{34}H_{31}NO_6$: 549.2151 Found: 549.2129.

COSY Spectrum of *M*-**33** shows the presence of a camphanate proton with a chemical shift coincident with the *tert*-butyl singlet at 1.47 ppm, confirming the integration of 10H:



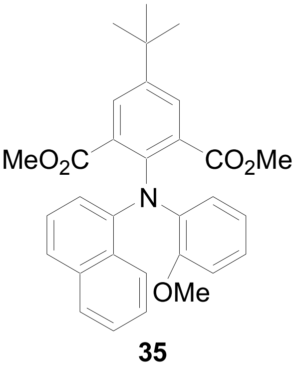
COSY Spectrum of *P*-**33** shows no evidence of a coincident camphanate proton at 1.47 ppm:





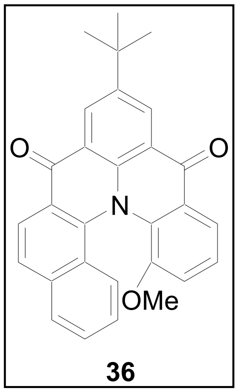
34

(2-Methoxy-phenyl)-naphthalen-1-yl-amine (34). 2-iodoanisole (6.50 mL, 50 mmol), 1-aminonaphthalene (7.16 g, 50 mmol), $Pd_2(dba)_3$ (0.916 g, 1.0 mmol), DPPF (0.832 g, 1.5 mmol), and sodium *tert*-butoxide (7.21 g, 75 mmol) were combined in a 100 mL Schlenk flask under argon. Dry toluene (30 mL) was added and the reaction vessel sealed. The reaction was heated to 110 °C for 18 h. The reaction was filtered and the filtrated washed with water and the organic layer removed using a separatory funnel. The aqueous layer was washed with three, 10 mL portions of toluene. The combined organic layers were dried over sodium sulfate, filtered, and the toluene removed by rotary evaporation. The residue was then purified by flash chromatography using 3:1 hexane/ethyl acetate as the eluent. The product was then recrystallized from dichloromethane/hexane to give 8.24 g of **34** (66% yield). ^1H NMR: ($CDCl_3$, 300 MHz) δ 3.95 (s, 3H), 6.48 (bs, 1H), 6.84 (m, 2H), 6.93 (m, 1H), 7.04 (m, 1H), 7.45 (m, 4H), 7.56 (d, J = 7.7, 1H), 7.86 (m, 1H), 8.06 (m, 2H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 55.7, 110.4, 114.7, 116.1, 119.4, 120.9, 122.0, 122.9, 125.6, 126.0, 126.1, 128.2, 128.4, 134.4, 134.7, 138.4, 148.0. HRMS Calcd For $C_{17}H_{15}NO$: 249.1154 Found: 249.1157.



35

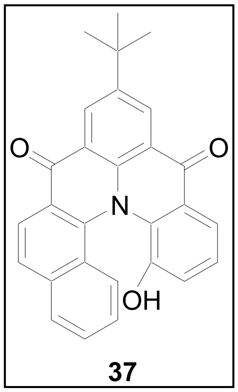
35. (2-Methoxy-phenyl)-naphthalen-1-yl-amine (**34**) (3.74 g, 15 mmol), 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester (4.94 g, 15 mmol), copper (0.095 g, 1.5 mmol), copper (I) iodide (0.189 g, 0.99 mmol), and potassium carbonate (3.11 g, 22.5 mmol) were combined in a 50 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser. 25 mL of di-*n*-butyether was added and the reaction heated to 150 °C under argon for 96 h. The solvent was distilled of and the residue was filtered using dichloromethane as a wash solvent. The filtrate was reduced by rotary evaporation and the residue was then purified by flash chromatography using 3:1 hexane/ethyl acetate as the eluent to give 2.25 g of **35** (30% yield). ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 1.33 (s, 9H), 2.91 (s, 3H), 3.28 (s, 3H), 3.44 (s, 3H), 6.70 (m, 2H), 6.87 (dd, *J* = 8.0 and 1.3 Hz, 1H), 6.96 (dt, *J* = 7.0 and 1.9 Hz, 1H), 7.22 (m, 1H), 7.35 (t, *J* = 8.1, 2H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.55 (d, *J* =2.4 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 31.1, 34.5, 51.6, 51.7, 113.8, 120.9, 123.8, 124.1, 124.6, 124.9, 125.3, 125.4, 125.5, 125.8, 128.0, 128.7, 128.9, 129.5, 130.0, 130.2, 134.7, 137.5, 143.4, 144.1, 146.3, 152.0, 168.7, 168.9. HRMS Calcd For $C_{31}H_{31}NO_5$: 497.2202 Found: 497.2196.



36

36. Compound **35** (2.96 g, 6.0 mmol) and NaOH (2.38 g, 60 mmol) was heated to reflux in 40 mL of 1:1 ethanol/water for 22 h. Ethanol was removed by rotary evaporation, diluted with 10 mL of water, and acidified with concentrated hydrochloric acid. The resulting precipitate was collected by vacuum filtration and washed with copious portions of distilled water. The solid was dried in a 80 °C oven for 12 h to give 2.41 g of the diacid of **35** (84% yield).

The diacid (1.63 g, 3.4 mmol) was dispersed in 25 mL of dry dichloromethane in a 50 mL, 3-neck round bottom flask equipped with a magnetic stir bar and reflux condenser. Under an argon atmosphere, a few drops of DMF was added, followed by oxalyl chloride (0.65 mL, 7.4 mmol). The reaction was heated to reflux for 0.5 h, cooled slightly, and $SnCl_4$ (0.85 mL, 7.4 mmol) added. The reaction was heated to reflux for an additional 2 h, cooled to room temperature, and added dropwise to 50 mL of a 1M aqueous solution of NaOH. The aqueous layer was washed with several portions of dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The residue was then purified by flash chromatography using dichloromethane as the eluent, to give 1.186 g of **36** (79% yield). ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 1.49 (s, 9H), 2.82 (s, 3H), 6.95 (dd, *J* = 8.2 and 1.3 Hz, 1H), 7.20 (dt, *J* = 7.1 and 1.3 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.54 (dt, *J* = 6.9 and 1.1 Hz, 1H), 7.83 (d, *J* = 8.3, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 8.09 (dd, *J* = 7.9 and 1.4 Hz, 1H), 8.40 (d, *J* = 8.6 Hz, 1H), 8.71 (d, *J* = 2.4 Hz, 1H), 8.76 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 31.4, 35.1, 55.0, 116.1, 119.1, 121.7, 123.0, 123.2, 123.8, 124.2, 125.2, 125.4, 125.5, 126.6, 127.9, 128.1, 128.6, 128.9, 129.1, 132.6, 134.8, 139.1, 140.8, 147.4, 150.1, 179.3, 180.1. HRMS Calcd For $C_{29}H_{23}NO_3$: 433.1678 Found: 433.1679.

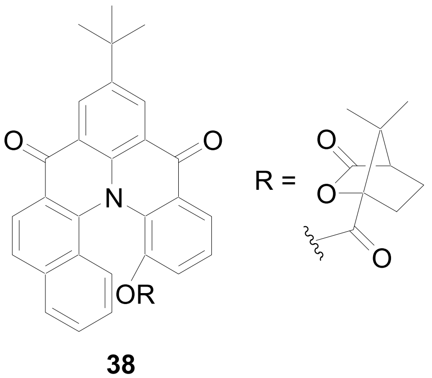


37

37. Compound **36** (1.057 g, 2.4 mmol) was heated to reflux in 60 mL of 1:2 mixture of acetic acid/hydrobromic acid for 90 h. The reaction was poured into 100 mL of water and filtered. The filtrate was extracted with several portions of dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and the solvent removed by rotary evaporation. The solvent was removed by rotary evaporation and the residue was then purified by flash chromatography using 20:1 dichloromethane/ethyl acetate as the eluent, to give 0.721 g of **37** (72% yield). ^{1}H NMR: (DMSO-d_6, 300 MHz) δ 1.96 (s, 9H), 7.50 (d, *J* = 7.9, 1H), 7.73 (t, *J* = 7.2, 1H), 7.84 (t, *J* = 7.9, 1H), 8.06 (t, *J* = 7.9, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 2H), 8.49 (d, *J* = 7.8 Hz, 1H), 8.74 (d, *J* = 8.7 Hz, 1H), 9.10 (dd, *J* = 8.4 and 2.4 Hz, 2H), 9.32 (s, 1H). ^{13}C NMR: (DMSO-d_6, 300 MHz) δ 30.9, 34.5, 116.5, 120.3, 120.5, 122.0, 123.4, 123.5, 123.6, 125.1, 125.4, 126.0, 126.8, 127.4, 127.6, 127.8, 128.4, 130.7, 134.5, 138.5, 140.5, 146.3, 148.3, 177.9, 179.1. HRMS Calcd For $C_{28}H_{21}NO_3$: 419.1521 Found: 419.1526.

M-**37**: *M*-**38** (0.155 g, 0.26 mmol) was stirred in 10 mL of 1M aqueous NaOH for 3 h at room temperature. The solution was neutralized with 1M aqueous HCl and extracted with CH_2Cl_2 and then with Et_2O. The organic layers were dried over sodium sulfate, filtered, and reduced by rotary evaporation. Column chromatography using 10:1 CH_2Cl_2:Et_2O as the eluent gave 0.109 g (100% yield) of *M*-**37**. The proton NMR was identical to **37**.

P-**37**: *P*-**38** (0.157 g, 0.26 mmol) was stirred in 10 mL of 1M aqueous NaOH for 3 h at room temperature. The solution was neutralized with 1M aqueous HCl and extracted with CH_2Cl_2 and then with Et_2O. The organic layers were dried over sodium sulfate, filtered, and reduced by rotary evaporation. Column chromatography using 10:1 CH_2Cl_2:Et_2O as the eluent gave 0.088 g (81% yield) of *P*-**37**. The proton NMR was identical to **37**.



38

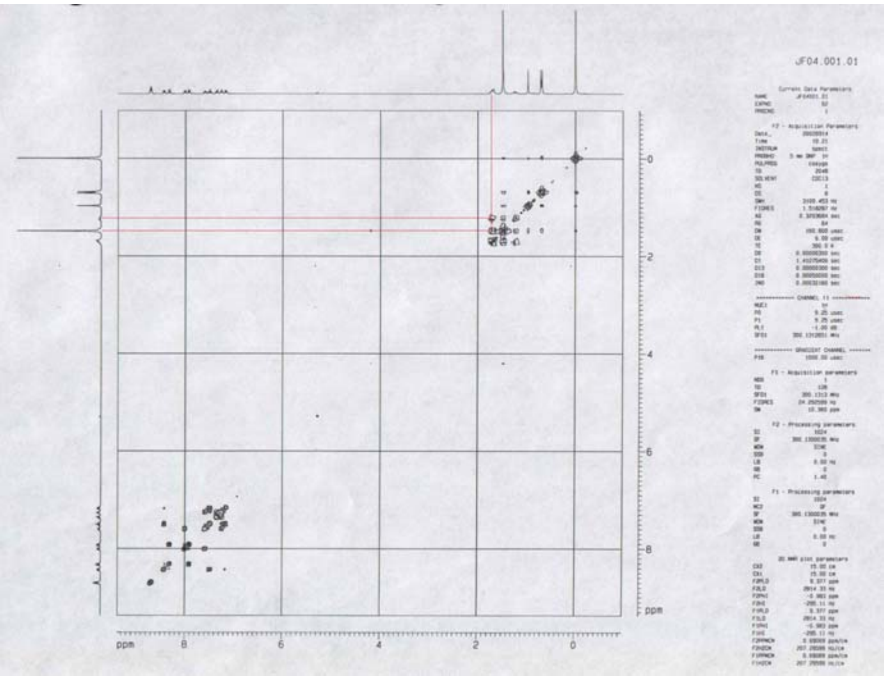
38. Compound **37** (1.054 g, 2.5 mmol) and DMAP (0.458 g, 3.8 mmol) were dissolved in 20 mL of dry dichloromethane. (1*S*)-camphanic chloride (1.083 g, 5.0 mmol) was added and the reaction heated to reflux for 1.5 h. Water (10 mL) was added, the organic layer removed using a separatory funnel and the aqueous layer washed with three, 10 mL portions of dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and the solvent removed by rotary evaporation. The residue was then purified by flash chromatography using 1:1

hexane/ethyl acetate as the eluent to give 0.843 g of *M*-**38** and 0.874 g of *P*-**38** (quantitative yield of **38**). Although this reaction has similar 2-D TLC characteristics as **33**, only a single column was necessary due to complete consumption of **37**.

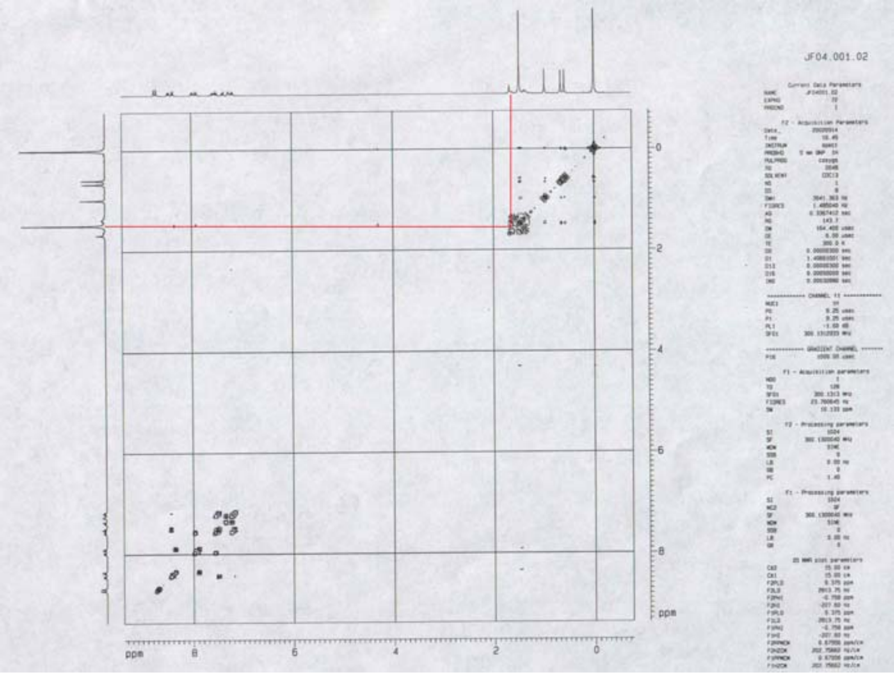
For *M*-**38**: ^{1}H NMR: (CDCl$_3$, 300 MHz) δ 0.68 (s, 3H), 0.71 (s, 3H), 0.97 (s, 3H), 1.24 (m, 1H), 1.49 (bs, 10H), 1.72 (m, 2H), 7.17 (dd, *J* = 7.9 and 1.5 Hz, 1H), 7.26 (t, *J* = 8.7 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 8.33 (d, *J* = 8.7 Hz, 1H), 8.44 (dd, *J* = 7.9 and 1.5 Hz, 1H), 8.71 (dd, *J* = 8.3 and 2.3 Hz, 2H). ^{13}C NMR: (CDCl$_3$, 300 MHz) δ 9.5, 16.3, 16.4, 28.5, 29.9, 31.3, 35.1, 54.4, 54.7, 89.4, 121.1, 123.7, 123.9, 124.0, 124.2, 125.3, 125.5, 125.7, 126.4, 127.1, 128.5, 128.9, 129.0, 129.2, 129.5, 136.0, 136.2, 139.0, 140.5, 147.9, 164.6, 177.2, 179.3, 179.5. HRMS Calcd For $C_{38}H_{33}NO_6$: 599.2308 Found: 599.2301.

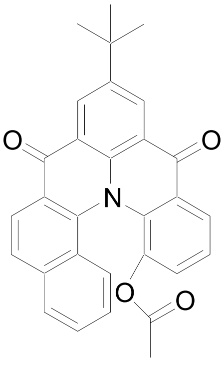
For *P*-**38**: ^{1}H NMR: (CDCl$_3$, 300 MHz) δ 0.59 (s, 3H), 0.66 (s, 3H), 0.98 (s, 3H), 1.36 (m, 2H), 1.48 (bs, 10H), 1.65 (m, 1H), 7.18 (dd, *J* = 7.9 and 1.3 Hz, 1H), 7.26 (m, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.45 (dd, *J* = 7.9 and 1.5 Hz, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.73 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR: (CDCl$_3$, 300 MHz) δ 9.5, 16.3, 16.6, 28.6, 30.0, 31.3, 35.1, 54.2, 54.4, 89.6, 122.1, 123.9, 124.1, 124.2, 124.3, 125.2, 125.4, 125.8, 126.1, 126.6, 127.5, 128.6, 128.7, 128.9, 129.1, 129.4, 135.7, 136.1, 139.1, 139.3, 140.5, 148.0, 164.7, 176.8, 179.1, 179.4. HRMS Calcd For $C_{38}H_{33}NO_6$: 599.2308 Found: 599.2311.

COSY Spectrum of *M*-**38** shows the presence of a camphanate proton with a chemical shift coincident with the *t*-butyl protons (singlet) at 1.49 ppm:



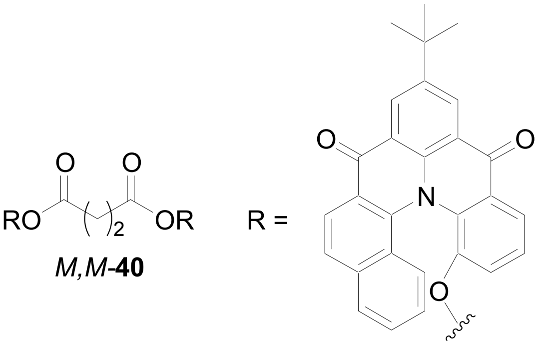
COSY Spectrum of *P*-**38** shows the presence of a camphanate proton with a chemical shift coincident with the *t*-butyl protons (singlet) at 1.48 ppm:





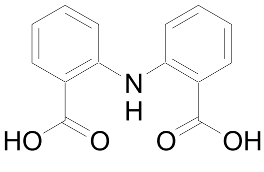
M-**39**

M-**39.** Malonic acid (5.6 mg, 0.05 mmol), *M*-**37** (45.2 mg, 0.11 mmol), DCC (24.5 mg, 0.12 mmol) and DMAP (11.0 mg, 0.09 mmol) were combined in a 50 mL round-bottom flask with 15 mL of CH_2Cl_2. The reaction was stirred 24 h at room temperature and then partition between water and CH_2Cl_2. The organic layers were collected and dried over sodium sulfate, filtered, and the solvent removed by rotary evaporation. The residue was then purified by flash chromatography using 10:1 CH_2Cl_2:Et_2O as the eluent to give 0.039 g (86% yield) of *M*-**39**. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 1.21 (s, 3H), 1.48 (s, 9H), 7.23 (dd, *J* = 7.9 and 1.3 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.42-7.49 (m, 2H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 8.37 (dd, *J* = 7.9 and 1.5 Hz, 1H), 8.41 (d, *J* = 8.7 Hz, 1H), 8.71 (dd, *J* = 2.4 and 8.7 Hz, 2H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 19.4, 31.3, 35.1, 121.8, 124.0, 124.1, 124.2, 125.0, 125.3, 125.8, 126.1, 126.4, 127.6, 128.4, 128.8, 128.9, 129.1, 129.2, 135.4, 135.6, 139.2, 140.8, 147.9, 166.8, 179.0, 179.7.



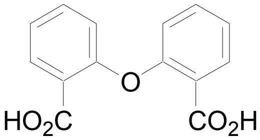
M,M-**40**

M,M-**40.** Succinyl chloride (0.03 mL, 0.26 mmol) was added to a solution of *M*-**37** (0.217 g, 0.52 mmol) and DMAP (0.063 g, 0.52 mmol) in 15 mL of CH_2Cl_2. The reaction was heated to reflux for 3 h and then reduced by rotary evaporation. The residue was purified by column chromatography using 10:1 CH_2Cl_2:Et_2O as the eluent to give 0.208 g (87% yield) of *M,M*-**40**. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 0.90 (t, *J* = 5.5 Hz, 2H), 1.48 (s, 18H), 7.06 (dd, *J* = 1.5 and 7.9 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.56 (7, *J* = 7.0 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H), 8.32 (dd, *J* = 1.5 and 7.9 Hz, 2H), 8.42 (d, *J* = 8.7 Hz, 2H), 8.67 (d, *J* = 2.4 Hz, 2H), 8.70 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR: (CDCl$_3$, 300 MHz) δ 26.7, 31.3, 35.1, 121.6, 123.8, 123.9, 124.0, 125.1, 125.3, 125.8, 125.9, 126.5, 127.5, 128.2, 128.9, 129.0, 129.2, 135.2, 135.5, 138.9, 140.4, 147.9, 168.0, 178.9, 179.5. HRMS Calcd For $C_{60}H_{45}N_2O_8$: 921.3176 Found: 921.3159.



41

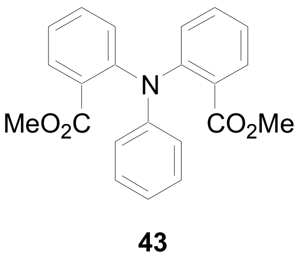
41. NaOH (10 eq) and **1** (1eq) were combined in a 1:1 mixture of ethanol:water and heated to reflux for 3 h. The ethanol was removed by rotary evaporation and the residue diluted with water and acidified with conc. HCl. The resulting precipitate was collected by vacuum filtration and recrystallized from ethanol to give **41** in quantitative yields. ^{1}H NMR: (DMSO, 300 MHz) δ 6.95 (t, *J* = 8.1 Hz, 2H), 7.41-749 (m, 4H), 7.91 (d, *J* = 7.3 Hz, 2H), 10.84 (bs, 1H), 13.03 (bs, 2H). Crystal data: $C_{14}H_{11}NO_4$, M = 251.27, monoclinic, space group *C* 2/*c* (No. 15), *a* = 13.1691 (7), *b* = 8.3651 (5), *c* = 11.7215 (5) Å, *V* = 1208.38 (11) Å^3, T = 298 K, Z = 4, μ = 0.11 mm^{-1}, 2456 reflections measured, 1387 unique (R$_{int}$ = 0.027), R_1 = 0.0582 (all data), wR_2 = 0.1305 (all data). Carbonyl groups assigned by C-O bond lengths.



42

42. Bis(2-methyl-phenyl)ether (0.269 g, 1.4 mmol), $KMnO_4$ (0.645 g, 4.1 mmol), and NaOH (1.09 g, 27.2 mmol) were combined in 50 mL water and heated to reflux for 2 h. The reaction was cooled to room temperature and 10 mL of EtOH was added. The reaction was filtered through celite and the filtrate acidified with concentrated HCl. Slow evaporation gave 0.285 g (80% yield) as a crystalline solid. Crystal data: $C_{14}H_{10}NO_5$, M=258.23, monoclinic, space group *C* 2/*c* (no. 15), *a* = 13.5889 (5), *b* = 6.6994 (3), *c* = 13.5648 (6) Å, *V* = 1217.39 (9)

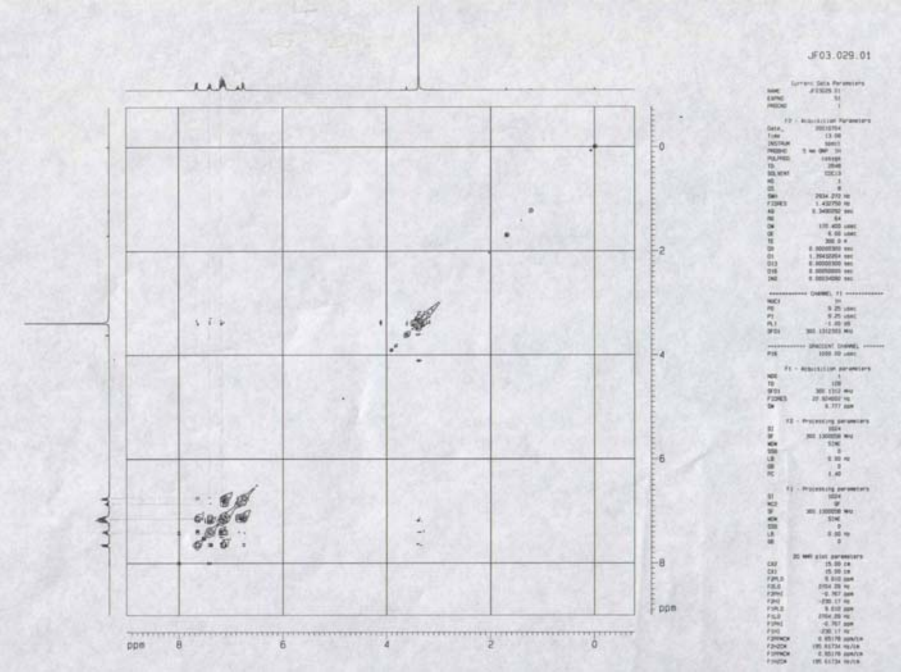
Å^3, T = 298 K, Z = 4, μ = 0.11 mm^{-1}, 1972 reflections measured, 1057 unique (R_{int} = 0.031), R_1 = 0.0632 (all data)], wR_2 = 0.1455 (all data). Carbonyl groups assigned by C-O bond lengths.

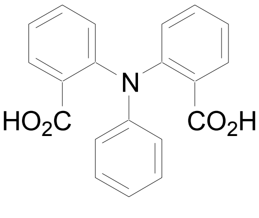


43

43. Aniline (2.28 mL, 25 mmol), methyl 2-iodobenzoate (11.18 mL, 52.5 mmol), K_2CO_3 (7.26 g, 52.5 mmol), Cu (0.33 g, 5.2 mmol) and CuI (0.22 g, 1.2 mmol) were combined in a 50 mL round-bottom flask with 15 mL of di-*n*-butylether and heated to 175 °C of 48 h. The solvent was removed by vacuum distillation and the residue taken up in CH_2Cl_2, filtered, and reduced by rotary evaporation. Column chromatography using 4:1 Hexane:EtOAc as the eluent followed by recrystallization from EtOH gave 7.321 g (81% yield) of **43**. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 6.76 (d, *J* = 7.9, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 7.15 (m, 6H), 7.41 (dt, *J* = 1.9 and 8.3 Hz, 2H), 7.67 (dd, *J* = 1.9 and 7.9 Hz, 2H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 51.7, 120.6, 121.6, 123.9, 127.8, 128.6, 128.8, 130.8, 132.6, 146.3, 148.4, 167.8. Anal. Calcd for $C_{22}H_{19}NO_4$: C = 73.12; H = 5.30; N = 3.88. Found: C = 72.65; H = 5.31; N = 3.71.

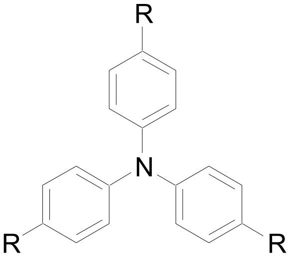
COSY NMR (300 MHz, $CDCl_3$):



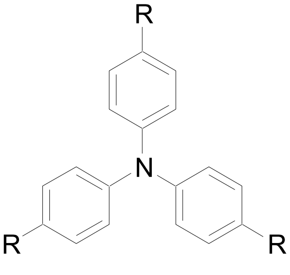


44

44. NaOH (4.0 g, 100 mmol) and **43** (3.61 g, 10 mmol) were combined in a 1:1 mixture of EtOH:H_2O and heated to reflux for 3 h. The EtOH was removed by rotary evaporation and the aqueous solution acidified with 1M HCl. The resulting precipitate was collected by vacuum filtration and oven dried to give 3.284 g (99% yield) of **44**. Crystals were obtained by slow evaporation of an acetone/water solution. ^{1}H NMR: (DMSO, 300 MHz) δ 7.25 (dd, *J* = 1.1 and 8.7, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.50 (dd, *J* = 0.9 and 8.3 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 2H), 7.72 (td, *J* = 1.7 and 7.7 Hz, 2H), 7.96 (dd, *J* = 1.7 and 7.3 Hz, 1H), 7.99 (dd, *J* = 1.7 and 7.3 Hz, 1H), 8.29 (dd, *J* = 1.7 and 7.9 Hz, 2H), 12.04 (bs, 2H). ESI-MS: 334.3. Crystal data: $C_{20}H_{15}NO_4$, M=333.34, monoclinic, space group $P\ 2_1/c$ (no. 14), a = 9.2755 (2), b = 10.7912 (4), c = 16.7186 (4) Å, V = 1658.61 (8) Å^3, T = 298 K, Z = 4, μ = 0.09 mm^{-1}, 5471 reflections measured, 2901 unique (R_{int} = 0.034), R_1 = 0.0539 (all data), wR_2 = 0.1138 (all data). Carbonyl groups assigned by C-O bond lengths.


45, R = CO_2Me

***4,4',4''*-amino-trisbenzoic acid-trimethylester (45).** Methyl 4-iodobenzoate (1.729 g, 6.6 mmol), methyl 4-aminobenzoate (0.454 g, 3.0 mmol), DPPF (0.274 g, 0.5 mmol), $Pd_2(dba)_3$ (0.302 g, 0.33 mmol), and *tert*-BuONa (0.721 g, 7.5 mmol) were all combined in a 50 mL Schlenk flask. Air was removed by vacuum and replaced with argon. 20 mL of dry toluene was added and the reaction heated to 110 °C for 12 h. The reaction was then filtered through cotton wool and partitioned between toluene and water. The organic layers were collected, dried over sodium sulfate, and reduced by rotary evaporation. Column chromatography in 3:1 hexane:EtOAc gave 0.995 g (76% yield) of **45**. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 3.91 (s, 9H), 7.13 (d, *J* = 8.7 Hz, 6H), 7.96 (d, *J* = 8.7 Hz, 6H). ^{13}C NMR: ($CDCl_3$, 300 MHz) δ 52.1, 123.8, 125.5, 131.2, 150.4, 166.4.


46, R = CO_2H

***4,4',4''*-amino-trisbenzoic acid (46).** NaOH (1.0 g, 25 mmol) and 45 (0.216 g, 0.51 mmol) were combined in a 1:1 mixture of EtOH:H_2O and heated to reflux for 2 h. The EtOH was removed by rotary evaporation and the aqueous solution acidified with 1M HCl. The resulting precipitate was collected by vacuum filtration and oven dried to give 0.189 g (98% yield) of **46**. Crystal data: $C_{21}H_{15}NO_6 \cdot C_7H_{10}N_2$, *M* = 499.523, Monoclinic, *C* 2/c, *a* = 31.9871(11) Å, *b* = 9.8128(4) Å, *c* = 19.5126(10) Å, α = 90.00o, β = 120.416(2)°, γ= 90.00°,*V* = 5281.7(4)Å^3, *Z* = 6, μ = 0.067 mm^{-1}, T = 298 K, data/parameters = 2350/334, converging to R_1 = 0.1164, wR_2 = 0.3185 (on 1547, $I > 2\sigma(I)$ observed data); R_1 = 0.1567, wR_2 = 0.3443 (all data), residual electron density: 1.787 e/Å^3.

BIBLIOGRAPHY

(1) Aliev, A. E.; MacLean, E. J.; Harris, K. D. M.; Kariuki, B. M.; Glidewell, C. "Dynamics of the hydrogen-bonding arrangement in solid triphenylmethanol: An investigation by solid-state H-2 NMR spectroscopy" *J. Phys. Chem. B* **1998**, *102*, 2165-2175.

(2) Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. "From molecules to materials: Current trends and future directions" *Adv. Mater.* **1998**, *10*, 1297-1336.

(3) Allinson, G.; Bushby, R. J.; Paillaud, J. L.; Thorntonpett, M. "Synthesis of a Derivative of Triangulene - the First Non-Kekule Polynuclear Aromatic" *J. Chem. Soc. Perkin Trans. 1* **1995**, 385-390.

(4) Almeida, M. H., R. T. "Handbook of Organic Conductive Molecules and Polymers*" Handbook of Organic Conductive Molecules and Polymers Vol. 1*; Nalwa, H. S.; John Wiley & Sons: New York, **1997**, 87-149.

(5) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. "Functionalized pentacene: Improved electronic properties from control of solid-state order" *J. Am. Chem. Soc.* **2001**, *123*, 9482-9483.

(6) Atkins, P. "Physical Chemistry*"* 5th ed.; W. H. Freeman and Company: New York, **1994**.

(7) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. "A well-resolved ice-like (H2O)(8) cluster in an organic supramolecular complex" *J. Am. Chem. Soc.* **2001**, *123*, 7192-7193.

(8) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. "Tailored porous materials" *Chem. Mater.* **1999**, *11*, 2633-2656.

(9) Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. "New triarylamine-containing polymers as hole transport materials in organic light-emitting diodes: Effect of polymer structure and cross-linking on device characteristics" *Chem. Mater.* **1998**, *10*, 1668-1676.

(10) Benin, V. A.; Martin, J. C.; Willcott, M. R. "Solution and solid state studies of some new silicon and germanium compounds stabilized by tridentate ligands" *Tetrahedron* **1997**, *53*, 10133-10154.

(11) Bilton, C.; Allen, F. H.; Shields, G. P.; Howard, J. A. K. "Intramolecular hydrogen bonds: common motifs, probabilities of formation and implications for supramolecular organization" *Acta Crystallogr. Sect. B* **2000**, *56*, 849-856.

(12) Bolognesi, A.; Botta, C.; Facchinetti, D.; Jandke, M.; Kreger, K.; Strohriegl, P.; Relini, A.; Rolandi, R.; Blumstengel, S. "Polarized electroluminescence in double-layer light-emitting diodes with perpendicularly oriented polymers" *Adv. Mater.* **2001**, *13*, 1072-1075.

(13) Boucher, E.; Simard, M.; Wuest, J. D. "Use of Hydrogen-Bonds to Control Molecular Aggregation - Behavior of Dipyridones and Pyridone-Pyrimidones Designed to Form Cyclic Triplexes" *J. Org. Chem.* **1995**, *60*, 1408-1412.

(14) Brickell, W. S.; Brown, A.; Kemp, C. M.; Mason, S. F. "pi-Electron Absorption and Circular Dichroism Spectra of [6]- and [7]-Helicene" *J. Chem. Soc.* **1971**, 756-760.

(15) Brown, A.; Kemp, C. M.; Mason, S. F. "Electronic Absorption, Polarised Excitation, and Circular Dichroism Spectra of [5]-Helicene (Dibenzo[*c,g*]phenanthrene)" *J. Chem. Soc.* **1971**, 751-755.

(16) Bruckner, C.; Powers, R. E.; Raymond, K. N. "Symmetry-driven rational design of a tetrahedral supramolecular Ti4L4 cluster" *Angew. Chem. Int. Ed.* **1998**, *37*, 1837-1839.

(17) Bushey, M. L.; Hwang, A.; Stephens, P. W.; Nuckolls, C. "Enforced stacking in crowded arenes" *J. Am. Chem. Soc.* **2001**, *123*, 8157-8158.

(18) Caronna, T.; Gabbiadini, S.; Mele, A.; Recupero, F. "Approaches to the azahelicene system: Synthesis and spectroscopic characterization of some diazapentahelicenes" *Helv. Chim. Acta* **2002**, *85*, 1-8.

(19) Caronna, T.; Sinisi, R.; Catellani, M.; Malpezzi, L.; Meille, S. V.; Mele, A. "Photochemical synthesis and structural properties of high membered thiohelicenes" *Chem. Commun.* **2000**, 1139-1140.

(20) Catellani, M.; Motti, E.; Ghelli, S. "Intramolecular benzylic C-H activation: palladium-catalyzed synthesis of hexahydromethanofluorenes" *Chem. Commun.* **2000**, 2003-2004.

(21) Caulder, D. L.; Raymond, K. N. "Supermolecules by design" *Acc. Chem. Res.* **1999**, *32*, 975-982.

(22) Caulder, D. L.; Raymond, K. N. "The rational design of high symmetry coordination clusters" *J. Chem. Soc. Dalton Trans.* **1999**, 1185-1200.

(23) Chen, B. L.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. "Interwoven metal-organic framework on a periodic minimal surface with extra-large pores" *Science* **2001**, *291*, 1021-1023.

(24) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. "Circularly polarized light generated by photoexcitation of luminophores in glassy liquid-crystal films" *Nature* **1999**, *397*, 506-508.

(25) Cheng, X. H.; Gao, Q. Y.; Smith, R. D.; Simanek, E. E.; Mammen, M.; Whitesides, G. M. "Characterization of hydrogen-bonded aggregates in chloroform by electrospray ionization mass spectrometry" *J. Org. Chem.* **1996**, *61*, 2204-2206.

(26) Conwell, E. M. "The Differences between One-Dimensional and 3-Dimensional Semiconductors" *Phys. Today* **1985**, *38*, 46-53.

(27) Dapperheld, S.; Steckhan, E.; Brinkhaus, K. H. G.; Esch, T. "Organic Electron-Transfer Systems .2. Substituted Triarylamine Cation-Radical Redox Systems - Synthesis, Electrochemical and Spectroscopic Properties, Hammet Behavior, and Suitability as Redox Catalysts" *Chem. Ber.* **1991**, *124*, 2557-2567.

(28) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J.; Meijer, E. W. "pi-conjugated oligomers and polymers with a self-assembled ladder-like structure" *J. Am. Chem. Soc.* **1996**, *118*, 8717-8718.

(29) Desiraju, G. R. "Hydration in Organic-Crystals - Prediction from Molecular-Structure" *Chem. Commun.* **1991**, 426-428.

(30) Desiraju, G. R. "Supramolecular Synthons in Crystal Engineering - a New Organic- Synthesis" *Angew. Chem. Int. Ed.* **1995**, *34*, 2311-2327.

(31) Diesveld, J. W.; Borkent, J. H.; Laarhoven, W. H. "The oxidation of hexahelicenes. Synthesis of hexahelicene-5,6-quinone" *Recl.Trav. Chim. Pays-Bas* **1980**, *99*, 391-394.

(32) Dopper, J. H.; Oudman, D.; Wynberg, H. "Use of thieno[2,3-b]thiophene in the synthesis of heterohelicenes by double photocyclizations" *J. Am. Chem. Soc.* **1973**, *95*, 3692-3698.

(33) Ducharme, Y.; Wuest, J. D. "Use of Hydrogen-Bonds to Control Molecular Aggregation - Extensive, Self-Complementary Arrays of Donors and Acceptors" *J. Org. Chem.* **1988**, *53*, 5787-5789.

(34) Dyker, G. "Palladium-Catalyzed C-H Activation of Methoxy Groups - a Facile Synthesis of Substituted 6h-Dibenzo B,D Pyrans" *Angew. Chem. Int. Ed.* **1992**, *31*, 1023-1025.

(35) Dyker, G. "Transition-Metal-Catalyzed Annelation Reactions .5. Palladium-Catalyzed C-H Activation of Tert-Butyl Groups - a Simple Synthesis of 1,2-Dihydrocyclobutabenzene Derivatives" *Angew. Chem. Int. Ed.* **1994**, *33*, 103-105.

(36) Dyreklev, P.; Berggren, M.; Inganas, O.; Andersson, M. R.; Wennerstrom, O.; Hjertberg, T. "Polarized Electroluminescence from an Oriented Substituted Polythiophene in a Light-Emitting Diode" *Adv. Mater.* **1995**, *7*, 43-45.

(37) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. "Modular chemistry: Secondary building units as a basis for the

design of highly porous and robust metal-organic carboxylate frameworks" *Acc. Chem. Res.* **2001**, *34*, 319-330.

(38) Ege, S. "Organic Chemistry - Structure and Reactivity" 3rd ed.; D. C. Heath and Company: Toronto, **1994**.

(39) Ermer, O.; Robke, C. "New Host Architecture of Hydroquinone with Enclathrated C-70" *J. Am. Chem. Soc.* **1993**, *115*, 10077-10082.

(40) Eskildsen, J.; Krebs, F. C.; Faldt, A.; Sommer-Larsen, P.; Bechgaard, K. "Preparation and structural properties of 7,8-dioxa 6 helicenes and 7a,14c-dihydro-7,8-dioxa 6 helicenes" *J. Org. Chem.* **2001**, *66*, 200-205.

(41) Etter, M. C. "Encoding and decoding hydrogen-bond patterns of organic compounds" *Acc. Chem. Res.* **1990**, *23*, 120-126.

(42) Faber, R.; Mielke, G. F.; Rapta, P.; Stasko, A.; Nuyken, O. "Anodic oxidation of novel hole-transporting materials derived from tetraarylbenzidines. Electrochemical and spectroscopic characterization" *Collect. Czech. Chem. Commun.* **2000**, *65*, 1403-1418.

(43) Ferguson, G.; Gallagher, J. F.; Glidewell, C.; Low, J. N.; Scrimgeour, S. N. "The Structure of Triphenylmethanol, Ph3coh" *Acta Crystallogr. Sect. C* **1992**, *48*, 1272-1275.

(44) Fey, H. J.; Kurreck, H.; Lubitz, W. "ENDOR studies of [6]helicene anion radical" *Tetrahedron* **1979**, *35*, 905-907.

(45) Field, J. E.; Combariza, M. Y.; Vachet, R. W.; Venkataraman, D. "Spontaneous assembly of a hydrogen-bonded tetrahedron" *Chem. Commun.* **2002**, 2260-2261.

(46) Field, J. E.; Venkataraman, D. "Heterotriangulenes - Structure and properties" *Chem. Mater.* **2002**, *14*, 962-964.

(47) Field, J. E.; Venkataraman, D. "Helix versus zig-zag: control of supramolecular topology via carboxylic acid conformations in ortho-substituted phenyl amines" *Chem. Commun.* **2002**, 306-307.

(48) Figuly, G. D.; Loop, C. K.; Martin, J. C. "Directed Ortho-Lithiation of Lithium Thiophenolate - New Methodology for the Preparation of Ortho-Substituted Thiophenols and Related-Compounds" *J. Am. Chem. Soc.* **1989**, *111*, 654-658.

(49) Fox, O. D.; Drew, M. G. B.; Beer, P. D. "Resorcarene-based nanoarchitectures: Metal-directed assembly of a molecular loop and tetrahedron" *Angew. Chem. Int. Ed.* **2000**, *39*, 135-140.

(50) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. "Molecular paneling via coordination" *Chem. Commun.* **2001**, 509-518.

(51) Gangopadhyay, P.; Radhakrishnan, T. P. "Helical superstructures of a C-2-symmetric molecule exhibiting strong second harmonic generation in the solid-state" *Angew. Chem. Int. Ed.* **2001**, *40*, 2451-2455.

(52) Gauthier, S.; Frechet, J. M. J. "Phase-Transfer Catalysis in the Ullmann Synthesis of Substituted Triphenylamines" *Synthesis* **1987**, 383-385.

(53) Gavezzotti, A.; Desiraju, G. R. "A Systematic Analysis of Packing Energies and Other Packing Parameters for Fused-Ring Aromatic-Hydrocarbons" *Acta Crystallogr. Sect. B* **1988**, *44*, 427-434.

(54) Geib, S. J.; Vicent, C.; Fan, E.; Hamilton, A. D. "A Self-Assembling, Hydrogen-Bonded Helix" *Angew. Chem. Int. Ed.* **1993**, *32*, 119-121.

(55) Graf, E.; Lehn, J. M. "Cryptates. XVII. Synthesis and cryptate complexes of a spheroidal macrotricyclic ligand with octahedrotetrahedral coordination" *J. Am. Chem. Soc.* **1975**, *97*, 5022-5024.

(56) Grell, M.; Bradley, D. D. C. "Polarized luminescence from oriented molecular materials" *Adv. Mater.* **1999**, *11*, 895-905.

(57) Groen, M. B.; Wynberg, H. "Optical Properties of Some Heterohelicenes. The Absolute Configuration" *J. Am. Chem. Soc.* **1971**, *93*, 2968-2974.

(58) Gujadhur, R.; Venkataraman, D. "Synthesis of diaryl ethers using an easy-to-prepare, air- stable, soluble copper(I) catalyst" *Synth. Commun.* **2001**, *31*, 2865-2879.

(59) Gujadhur, R.; Venkataraman, D.; Kintigh, J. T. "Formation of aryl-nitrogen bonds using a soluble copper(I) catalyst" *Tetrahedron Lett.* **2001**, *42*, 4791-4793.

(60) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. "Novel folding patterns in a family of oligoanthranilamides: Non-peptide oligomers that form extended helical secondary structures" *J. Am. Chem. Soc.* **1997**, *119*, 10587-10593.

(61) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. "Prominent gelation and chiral aggregation of alkylamides derived from trans-1,2-diaminocyclohexane" *Angew. Chem. Int. Ed.* **1996**, *35*, 1949-1951.

(62) Hanessian, S.; Simard, M.; Roelens, S. "Molecular Recognition and Self-Assembly by Non-Amidic Hydrogen- Bonding - an Exceptional Assembler of Neutral and Charged Supramolecular Structures" *J. Am. Chem. Soc.* **1995**, *117*, 7630-7645.

(63) Harrowven, D. C.; Nunn, M. I. T.; Fenwick, D. R. "5 Helicenes by iterative radical cyclisations to arenes" *Tetrahedron Lett.* **2002**, *43*, 3189-3191.

(64) Hartwig, J. F. "Carbon-heteroatom bond-forming reductive eliminations of amines, ethers, and sulfides" *Acc. Chem. Res.* **1998**, *31*, 852-860.

(65) Hartwig, J. F. "Transition metal catalyzed synthesis of arylamines and aryl ethers from aryl halides and triflates: Scope and mechanism" *Angew. Chem. Int. Ed.* **1998**, *37*, 2047-2067.

(66) Hellwinkel, D.; Aulmich, G.; Melan, M. "Modified tetrahelicene systems" *Chem. Ber.* **1976**, *109*, 2770-2784.

(67) Hellwinkel, D.; Melan, M. "Heteropolycyclic compounds of the triangulene type. I. 8,12-Dihydro-4H-benzo[1,9]quinolizino[3,4,5,6,7-difg]acridine-4,8,12-trione and 5,9-dihydroquino[3,2,1-de]acridine-5,9-dione" *Chem. Ber.* **1971**, *104*, 1001-1016.

(68) Hellwinkel, D.; Melan, M. "Heteropolycycles of the triangulene type. II. Stereochemistry of bridged triarylamines" *Chem. Ber.* **1974**, *107*, 616-626.

(69) Hellwinkel, D.; Schmidt, W. "Modified tetrahelicene systems. III. Doubly ortho-bridged triphenylamine derivatives" *Chem. Ber.* **1980**, *113*, 358-384.

(70) Hirschberg, J.; Brunsveld, L.; Ramzi, A.; Vekemans, J.; Sijbesma, R. P.; Meijer, E. W. "Helical self-assembled polymers from cooperative stacking of hydrogen-bonded pairs" *Nature* **2000**, *407*, 167-170.

(71) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J. "Molecular encapsulation" *Angew. Chem. Int. Ed.* **2002**, *41*, 1488-1508.

(72) Hoffmann, R.; Janiak, C.; Kollmar, C. "A Chemical Approach to the Orbitals of Organic Polymers" *Macromolecules* **1991**, *24*, 3725-3746.

(73) Janke, R. H.; Haufe, G.; Wurthwein, E. U.; Borkent, J. H. "Racemization barriers of helicenes: A computational study" *J. Am. Chem. Soc.* **1996**, *118*, 6031-6035.

(74) Jung, O. S.; Kim, Y. J.; Lee, Y. A.; Park, J. K.; Chae, H. K. "Smart molecular helical springs as tunable receptors" *J. Am. Chem. Soc.* **2000**, *122*, 9921-9925.

(75) Katz, T. J. "Syntheses of functionalized and aggregating helical conjugated molecules" *Angew. Chem. Int. Ed.* **2000**, *39*, 1921-1923.

(76) Katz, T. J.; Liu, L. B.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S. H.; Nuckolls, C.; Rickman, B. H. "An efficient synthesis of functionalized helicenes" *J. Am. Chem. Soc.* **1997**, *119*, 10054-10063.

(77) Kawata, H.; Niizuma, S. "Acid-Base-Equilibrium in Excited-State of 10-Methylacridone" *J. Prakt. Chem.-Chem. Ztg.* **1994**, *336*, 425-428.

(78) Kim, J.; Chen, B. L.; Reineke, T. M.; Li, H. L.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. "Assembly of metal-organic frameworks from large organic and inorganic secondary building units: New examples and simplifying principles for complex structures" *J. Am. Chem. Soc.* **2001**, *123*, 8239-8247.

(79) Kim, S. S.; Weissman, S. I. "Intersystem crossing in hexahelicene" *J. Am. Chem. Soc.* **1979**, *101*, 5863-5864.

(80) Kitahara, Y.; Tanaka, K. "Synthesis, crystal structure and properties of thiaheterohelicenes containing phenolic hydroxy functions" *Chem. Commun.* **2002**, 932-933.

(81) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J. "Self-assembly of molecular prisms via an organometallic "clip"" *Org. Lett.* **2002**, *4*, 913-915.

(82) Laali, K. K.; Houser, J. J. "Electrophilic and Oxidative Chemistry of 4-Methyl 6 Helicene, 6 Helicene and Coronene - Persistent Ion Generation in Superacid Media, Gas-Phase Mass-Spectrometric Studies and Am1 Calculations" *J. Chem. Soc. Perkin Trans. 2* **1994**, 1303-1308.

(83) Laarhoven, W. H.; Brus, G. J. M. "Polarographic Data and Deviations from Coplanarity of Helicene Molecules" *J. Chem. Soc.* **1971**, 1433-1434.

(84) Laarhoven, W. H.; Prinsen, W. J. C. "Carbohelicenes and Heterohelicenes" *Top. Curr. Chem.* **1984**, *125*, 63-130.

(85) Lai, Y. H. "Synthesis and Diatropicity of a Phenanthrene-Annelated Trans-Dimethyldihydropyrene - a Novel Molecule to Indicate the High Pi-Bond Order of the 9,10 Bond of Phenanthrene" *J. Am. Chem. Soc.* **1985**, *107*, 6678-6683.

(86) Larock, R. C. "Comprehensive Organic Transformations - A Guide to Fuctional Group Preparations*"*; VCH Publishers: New York, **1989**.

(87) Laursen, B. W.; Krebs, F. C. "Synthesis of a triazatriangulenium salt" *Angew. Chem. Int. Ed.* **2000**, *39*, 3432-3434.

(88) Laursen, B. W.; Krebs, F. C. "Synthesis, structure, and properties of azatriangulenium salts" *Chem.-Eur. J.* **2001**, *7*, 1773-1783.

(89) Laursen, B. W.; Krebs, F. C.; Nielsen, M. F.; Bechgaard, K.; Christensen, J. B.; Harrit, N. "2,6,10-Tris(dialkylamino)trioxatriangulenium ions. Synthesis, structure, and properties of exceptionally stable carbenium ions" *J. Am. Chem. Soc.* **1998**, *120*, 12255-12263.

(90) Lawrence, D. S.; Jiang, T.; Levett, M. "Self-Assembling Supramolecular Complexes" *Chem. Rev.* **1995**, *95*, 2229-2260.

(91) Leiserowitz, L. "Molecular Packing Modes. Carboxylic Acids" *Acta Crystallogr. Sect. B* **1976**, *32*, 775-802.

(92) Liberko, C. A.; Miller, L. L.; Katz, T. J.; Liu, L. B. "The Electronic-Structure of Helicene Bisquinone Anion Radicals" *J. Am. Chem. Soc.* **1993**, *115*, 2478-2482.

(93) Lightner, D. A.; Gurst, J. E. "Organic Conformational Analysis and Stereochemistry from Circular Dichroism Spectroscopy*" Methods in Stereochemical Analysis Vol.* Marchand, A. P.; John Wiley & Sons: New York, **2000**, 37-62.

(94) Lofthagen, M.; Vernonclark, R.; Baldridge, K. K.; Siegel, J. S. "Synthesis of Trioxatricornan and Derivatives - Useful Keystones for the Construction of Rigid Molecular Cavities" *J. Org. Chem.* **1992**, *57*, 61-69.

(95) Lovinger, A. J.; Nuckolls, C.; Katz, T. J. "Structure and morphology of helicene fibers" *J. Am. Chem. Soc.* **1998**, *120*, 264-268.

(96) Lu, J. J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. "Polygons and faceted polyhedra and nanoporous networks" *Angew. Chem. Int. Ed.* **2001**, *40*, 2113-2116.

(97) MacGillivray, L. R.; Atwood, J. L. "A chiral spherical molecular assembly held together by 60 hydrogen bonds" *Nature* **1997**, *389*, 469-472.

(98) MacGillivray, L. R.; Atwood, J. L. "Structural classification and general principles for the design of spherical molecular hosts" *Angew. Chem. Int. Ed.* **1999**, *38*, 1019-1034.

(99) MacGillivray, L. R.; Atwood, J. L. "Cavity-containing materials based upon resorcin 4 arenes by discovery and design" *J. Solid State Chem.* **2000**, *152*, 199-210.

(100) March, J. "Advanced Organic Chemistry-Reactions, Mechanisms, and Structure" 4th ed.; John Wiley & Sons: New York, **1992**.

(101) Marsella, M. J.; Kim, I. T.; Tham, F. "Toward conjugated double helical ladder polymers: Cyclooctatetrathiophene as a highly versatile double helical scaffold" *J. Am. Chem. Soc.* **2000**, *122*, 974-975.

(102) Meurer, K. P.; Vogtle, F. "Helical Molecules in Organic-Chemistry" *Top. Curr. Chem.* **1985**, *127*, 1-76.

(103) Montali, A.; Bastiaansen, G.; Smith, P.; Weder, C. "Polarizing energy transfer in photoluminescent materials for display applications" *Nature* **1998**, *392*, 261-264.

(104) Moulton, B.; Lu, J. J.; Mondal, A.; Zaworotko, M. J. "Nanoballs: nanoscale faceted polyhedra with large windows and cavities" *Chem. Commun.* **2001**, 863-864.

(105) Muci, A. R.; Buchwald, S. L. "Practical palladium catalysts for C-N and C-O bond formation",*Cross-Coupling Reactions, Vol. 219*, **2002**; pp 131-209.

(106) Murguly, E.; McDonald, R.; Branda, N. R. "Chiral discrimination in hydrogen-bonded 7 helicenes" *Org. Lett.* **2000**, *2*, 3169-3172.

(107) Namba, K.; Stubbs, G. "Structure of Tobacco Mosaic-Virus at 3.6-a Resolution - Implications for Assembly" *Science* **1986**, *231*, 1401-1406.

(108) Nelson, J. "Solar energy - Solar cells by self-assembly?" *Science* **2001**, *293*, 1059-1060.

(109) Newman, M. S.; Darlak, R. S.; Tsai, L. "Optical Properties of Hexahelicene" *J. Am. Chem. Soc.* **1967**, *89*, 6191-6193.

(110) Newman, M. S.; Lednicer, D. "The Synthesis and Resolution of Hexahelicene" *J. Am. Chem. Soc.* **1956**, *78*, 4765-4770.

(111) Newman, M. S.; Lutz, W. B.; Lednicer, D. "A New Reagent for Resolution by Complex Formation; The Resolution of Phenanthro-[3,4-c]Phenanthrene" *J. Am. Chem. Soc.* **1955**, *77*, 3420-3421.

(112) Norsten, T. B.; McDonald, R.; Brenda, N. R. "The self-assembly and spontaneous resolution of a hydrogen- bonded helix" *Chem. Commun.* **1999**, 719-720.

(113) Norsten, T. B.; Peters, A.; McDonald, R.; Wang, M. T.; Branda, N. R. "Reversible 7 -thiahelicene formation using a 1,2- dithienylcyclopentene photochrome" *J. Am. Chem. Soc.* **2001**, *123*, 7447-7448.

(114) Nuckolls, C.; Katz, T. J. "Synthesis, structure, and properties of a helical columnar liquid crystal" *J. Am. Chem. Soc.* **1998**, *120*, 9541-9544.

(115) Nuckolls, C.; Katz, T. J.; Castellanos, L. "Aggregation of conjugated helical molecules" *J. Am. Chem. Soc.* **1996**, *118*, 3767-3768.

(116) Nuckolls, C.; Katz, T. J.; Katz, G.; Collings, P. J.; Castellanos, L. "Synthesis and aggregation of a conjugated helical molecule" *J. Am. Chem. Soc.* **1999**, *121*, 79-88.

(117) Owens, L.; Thilgen, C.; Diederich, F.; Knobler, C. B. "A New Helicopodand - Molecular Recognition of Dicarboxylic- Acids with High Diastereoselectivity" *Helv. Chim. Acta* **1993**, *76*, 2757-2774.

(118) Paul, R. L.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Reeves, Z. R.; Ward, M. D. "Effects of metal co-ordination geometry on self-assembly: a dinuclear double helicate complex and a tetranuclear cage complex of a new bis-bidentate bridging ligand" *J. Chem. Soc. Dalton Trans.* **2000**, 845-851.

(119) Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H.; Meijer, E. W. "Circularly polarized electroluminescence from a polymer light-emitting diode" *J. Am. Chem. Soc.* **1997**, *119*, 9909-9910.

(120) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. "Synthesis and properties of an aggregating heterocyclic helicene" *J. Am. Chem. Soc.* **2001**, *123*, 11899-11907.

(121) Rajca, A.; Wang, H.; Bolshov, P.; Rajca, S. "A Greek cross dodecaphenylene: sparteine-mediated asymmetric synthesis of chiral D-2-symmetric pi-conjugated tetra-o- phenylenes" *Tetrahedron* **2001**, *57*, 3725-3735.

(122) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. "Annelated heptathiophene: A fragment of a carbon-sulfur helix" *Angew. Chem. Int. Ed.* **2000**, *39*, 4481-4483.

(123) Riehl, J. P.; Richardson, F. S. "Circularly Polarized Luminescence Spectroscopy" *Chem. Rev.* **1986**, *86*, 1-16.

(124) Riehl, J. P.; Richardson, F. S. "Circularly-Polarized Luminescence",*Metallobiochemistry, Part C, Vol. 226*, **1993**; pp 539-553.

(125) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. "Infinite secondary building units and forbidden catenation in metal-organic frameworks" *Angew. Chem. Int. Ed.* **2002**, *41*, 284-287.

(126) Rowan, A. E.; Nolte, R. J. M. "Helical molecular programming" *Angew. Chem. Int. Ed.* **1998**, *37*, 63-68.

(127) Rozen, S.; Dayan, S. "At last, 1,10-phenanthroline-N,N '-dioxide, a new type of helicene, has been synthesized using HOF center dot CH3CN" *Angew. Chem. Int. Ed.* **1999**, *38*, 3471-3473.

(128) Schmidt-Mende, L.; Fechtenkotter, A.; Mullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. "Self-organized discotic liquid crystals for high-efficiency organic photovoltaics" *Science* **2001**, *293*, 1119-1122.

(129) Selby, T. D.; Kim, K. Y.; Blackstock, S. C. "Patterned redox arrays of polyarylamines I. Synthesis and electrochemistry of a p-phenylenediamine and arylamino-appended p-phenylenediamine arrays" *Chem. Mater.* **2002**, *14*, 1685-1690.

(130) Seo, D. K.; Hoffmann, R. "Direct and indirect band gap types in one-dimensional conjugated or stacked organic materials" *Theor. Chem. Acc.* **1999**, *102*, 23-32.

(131) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. "Anodic Oxidation Pathways of Aromatic Amines. Electrochemical and Electron Paramagnetic Resonance Studies" *J. Am. Chem. Soc.* **1966**, *88*, 3498-3503.

(132) Shapiro, R.; Slobodin, D. "Synthesis of the dibenzo[b,g]oxocin system" *J. Org. Chem.* **1969**, *34*, 1165-1168.

(133) Shirota, Y. "Organic materials for electronic and optoelectronic devices" *J. Mater. Chem.* **2000**, *10*, 1-25.

(134) Silverstein, R. M.; Webster, F. X. "Spectrometric Identification of Organic Compounds" 6th ed.; John Wiley & Sons: New York, **1998**.

(135) Staab, H. A.; Diehm, M.; Krieger, C. "Synthesis, Structure and Basicity of 1,16-Diaza 6 Helicene" *Tetrahedron Lett.* **1994**, *35*, 8357-8360.

(136) Stang, P. J.; Olenyuk, B. "Self-assembly, symmetry, and molecular architecture: Coordination as the motif in the rational design of supramolecular metallacyclic polygons and polyhedra" *Acc. Chem. Res.* **1997**, *30*, 502-518.

(137) Tanaka, H.; Ogashiwa, S.; Kawazura, H. "Electron spin resonance of thiaheterohelicene radical anions" *Chem. Lett.* **1981**, *5*, 585-588.

(138) Tanaka, K.; Kitahara, Y. "Self-assembly of (P)-heterohelicenediol into a four-leaf clover motif" *Chem. Commun.* **1998**, 1141-1142.

(139) Tanaka, K.; Osuga, H.; Kitahara, Y. "Elongation and contraction of molecular springs. Synthesis, structures, and properties of bridged 7 thiaheterohelicenes" *J. Org. Chem.* **2002**, *67*, 1795-1801.

(140) Tashiro, M.; Yamato, T. "Studies on selective preparation of aromatic compounds. Part 16. A convenient preparation of 1,2-di- and 1,2,3-trisubstituted benzenes using the tert-butyl function as a positional protective group" *J. Chem. Soc. Perkin Trans. 1* **1972**, 176-179.

(141) Terpin, A. J.; Ziegler, M.; Johnson, D. W.; Raymond, K. N. "Resolution and kinetic stability of a chiral supramolecular assembly made of labile components" *Angew. Chem. Int. Ed.* **2001**, *40*, 157-160.

(142) Thongpanchang, T.; Paruch, K.; Katz, T. J.; Rheingold, A. L.; Lam, K. C.; Liable-Sands, L. "Why (1S)-camphanates are excellent resolving agents for helicen-1-ols and why they can be used to analyze absolute configurations" *J. Org. Chem.* **2000**, *65*, 1850-1856.

(143) Treboux, G.; Lapstun, P.; Wu, Z. H.; Silverbrook, K. "Electronic conductance of helicenes" *Chem. Phys. Lett.* **1999**, *301*, 493-497.

(144) Urry, D. W. "Molecular Machines - How Motion and Other Functions of Living Organisms Can Result from Reversible Chemical-Changes" *Angew. Chem. Int. Ed.* **1993**, *32*, 819-841.

(145) Vaillancourt, L.; Simard, M.; Wuest, J. D. "Synthesis and self-association of 4-pyrimidinones" *J. Org. Chem.* **1998**, *63*, 9746-9752.

(146) Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. "Strong enhancement of nonlinear optical properties through supramolecular chirality" *Science* **1998**, *282*, 913-915.

(147) Weck, M.; Dunn, A. R.; Matsumoto, K.; Coates, G. W.; Lobkovsky, E. B.; Grubbs, R. H. "Influence of perfluoroarene-arene interactions on the phase behavior of liquid crystalline and polymeric materials" *Angew. Chem. Int. Ed.* **1999**, *38*, 2741-2745.

(148) Wegner, G. "Polymers with Metal-Link Conductivity-Preview of their Synthesis, Structure and Properties" *Angew. Chem. Int. Ed.* **1981**, *20*, 361-381.

(149) Weigang, O. E.; Turner, J. A.; Trouard, P. A. "Emission Polarization and Circular Dichroism of Hexahelicene" *J. Chem. Phys.* **1966**, *45*, 1126-1134.

(150) Weissman, S. I.; Chang, R. "Optical and magnetic properties of anions of hexahelicene" *J. Am. Chem. Soc.* **1972**, *94*, 8683-8685.

(151) Weix, D. J.; Dreher, S. D.; Katz, T. J. "5 HELOL phosphite: A helically grooved sensor of remote chirality" *J. Am. Chem. Soc.* **2000**, *122*, 10027-10032.

(152) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. "Molecular Self-Assembly and Nanochemistry - a Chemical Strategy for the Synthesis of Nanostructures" *Science* **1991**, *254*, 1312-1319.

(153) Wynberg, H.; Groen, M. B. "Synthesis, Resolution, and Optical Rotary Dispersion of a Hexa- and a Heptaheterohelicene" *J. Am. Chem. Soc.* **1968**, *90*, 5339-5341.

(154) Yaghi, O. M.; Li, H. L.; Davis, C.; Richardson, D.; Groy, T. L. "Synthetic strategies, structure patterns, and emerging properties in the chemistry of modular porous solids" *Acc. Chem. Res.* **1998**, *31*, 474-484.

(155) Yamada, K.-I.; Tanaka, H.; Nakagawa, H.; Ogashiwa, S.; Kawazura, H. "NMR and CD Spectral Features of Thiaheterohelicenes. Effect of Intramolecular Overlap of Aromatic Rings" *Bull. Chem. Soc. Jpn.* **1982**, *55*, 500-503.

(156) Yang, B. H.; Buchwald, S. L. "Palladium-catalyzed amination of aryl halides and sulfonates" *J. Organomet. Chem.* **1999**, *576*, 125-146.

(157) Yang, B. W.; Liu, L. B.; Katz, T. J.; Liberko, C. A.; Miller, L. L. "Electron Delocalization in Helical Quinone Anion Radicals" *J. Am. Chem. Soc.* **1991**, *113*, 8993-8994.

(158) Yoshifuji, M.; Nakazawa, M.; Sato, T.; Toyota, K. "Formation and rearrangement of dithioxo- and diselenoxophosphoranes carrying bulky 4-t-butyl-2,6-bis(methoxyalkyl)phenyl groups" *Tetrahedron* **2000**, *56*, 43-55.

(159) Zhu, J.; Parra, R. D.; Zeng, H. Q.; Skrzypczak-Jankun, E.; Zeng, X. C.; Gong, B. "A new class of folding oligomers: Crescent oligoamides" *J. Am. Chem. Soc.* **2000**, *122*, 4219-4220.

(160) Zucca, A.; Cinellu, M. A.; Pinna, M. V.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. "Cyclopalladation of 6-substituted-2,2 '-bipyridines. Metalation of unactivated methyl groups vs aromatic C-H activation" *Organometallics* **2000**, *19*, 4295-4304.